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AND THE

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MINERALOGY OF A URANINITE DEPOSIT AT CARIBOU, COLORADO.

HAROLD D. WRIGHT.

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ABSTRACT.

At the Caribou mine, near Nederland, Colorado, a vein of uraninite-bearing sulfide ore in monzonite is enveloped by an alteration halo up to

four feet thick. Alteration began with the development of chlorite, calcite, epidote, and pyrite in pyroxene and biotite followed by an argillic phase of montmorillonite and kaolinite formation chiefly in plagioclase and orthoclase, and finally a sericitic and silicic phase strongly developed adjacent to the vein. The zonal arrangement is complicated by a sericitized zone lying outside the argillized zone. The alteration was reflected chemically by strong leaching of lime and soda, increases in potash and silica adjacent to the vein, and little change in magnesia and alumina.

Deposition of vein minerals took place in two stages separated by a period of brecciation. In Stage A, quartz, calcite, and siderite were followed successively by pyrite, chalcopyrite, sphalerite, and galena. Uraninite was deposited early in Stage B, following gersdorffite and chalcedony. Sphalerite, chalcopyrite, pyrite, argentite, proustite, and native silver completed the sequence. Uranium leakage from the vein extended to the outer limit of altered wall rock, beyond lead and zinc dissemination. The metals appear to have been transported by ionic diffusion through porous wall rock, and penetration was controlled by the amount of porous rock formed by hydrothermal alteration, rather than by abundance and spacing of fractures.

Uraninite at Caribou has characteristic colloform texture, and a colloidal origin appears probable. Sulfides showing similar forms are believed not to have had a colloidal origin. Measurement of the three best x-ray powder patterns of uraninite gave lattice constant values of 5.368 A°, 5.385 A°, and 5.398 A°. The variation may be due to differences in U^{6}/total U ratio in the three different specimens.

INTRODUCTION.

DURING the summer of 1949 the writer visited several primary vein uranium deposits in Colorado and Ontario which were being actively explored as possible uranium sources. A group of vein and wall rock samples was collected at each deposit to provide material for a detailed mineralogical study. The purpose of this study was to gain more information concerning the mineralogy of primary vein deposits of uranium, particularly along the lines of wall rock alteration, distribution of uranium in the wall rock, paragenesis and spatial relations of vein minerals, and the physical and structural character of uraninite.

The Caribou Mine is located in Boulder County in the Colorado Front Range, four miles west of the town of Nederland and about 35 miles northwest of Denver. Uranium was discovered at the Caribou Mine in 1945 by G. C. Ridland (21) [1] during a Geiger counter survey of the dump and underground workings. Prior to the discovery of uranium the mine had intermittently been worked for silver ores since 1869. The ores, which also contained important amounts of lead and some zinc, were localized along two sets of fractures cutting the interior portion of a stock-shaped intrusive. One set of fractures strikes east and the other northeast; most members of both sets dip steeply to the north, at angles of 70 to 90 degrees. The ores are found along certain members of both sets, and are especially rich at intersections.

The Caribou stock is elongated north-south and is approximately one and three-quarters miles long and about a mile wide. The predominant rock type

[1] Numbers in parentheses refer to Bibliography at end of paper.

has been described variously as a quartz monzonite (1, p. 44), and an orthoclase-biotite gabbro (10). As pointed out by Bastin and Hill, and later by W. Smith (28), several distinct rock types with gradational boundaries make up the intrusive mass. The stock is one of a group of intrusive bodies in the Algonkian granite and schist comprising the core of the Front Range. The intrusives cut Cretaceous sedimentary rocks, and are described by Lovering (16) and by Lovering and Goddard (17) as early Eocene.

Since a detailed field study of the Caribou deposit has been made by the U. S. Geological Survey, the present study has been primarily a laboratory investigation. Field work was limited to a brief examination and the collection of samples. The work was conducted as part of a program of mineralogical studies of uraninite and uraninite deposits in progress at Columbia University under the sponsorship of the Atomic Energy Commission.

SAMPLING.

The uraninite-bearing vein (14) at the Caribou Mine, known as the "Radium Vein," is an offshoot from a larger silver-bearing vein, the "No-Name Vein," in which significant amounts of uranium have not been discovered. The No-Name Vein strikes generally northeast and dips steeply to the north; the Radium Vein strikes east and dips 70 to 90 degrees north. The uranium-bearing portion of the Radium Vein has a width of generally less than one inch but swells at intervals to a breadth of six inches, and the vein is enclosed by an alteration halo several feet in thickness. Radioactive showings have been found on both the 920 and 1040 levels, but the best exposures are on the 1040 level and along a raise and a winze following the vein from the 1040 level.

Samples were taken at several places along the 920 level, and along three lines of section across the vein, in the raise above the 1040 level. Each alteration band along the section lines was sampled, as well as the vein and the fresh wall rock where exposed. The positions of the sampling lines and samples relative to the vein are shown in Figure 1.

WALL ROCK OF THE RADIUM VEIN.

The Fresh Rock.

In one of the early studies of the Caribou stock, Jennings (10) found the body to be gabbroic throughout, with the marginal phase differing slightly from the interior portion in composition and texture, but with quartz absent throughout. He described the interior portion (in the zone of silver mineralization) as composed of an orthoclase-biotite gabbro. Bastin and Hill (1, p. 44), in a more detailed study, found a wide variety of rocks, of which quartz monzonite, monzonite, olivine monzonite, gabbro, hornblende gabbro, and pyroxenite are the most abundant. They attribute the wide variety of rocks to a differentiation of the original magma, which they believe to have had a composition close to the predominate "quartz monzonite" phase. In a more recent, detailed study, W. Smith (28) confirmed the wide variety of rock types

described by Bastin and Hill but was led to the conclusion that the composite mass was formed from separate, successive intrusions of varying composition rather than by differentiation from a homogeneous magma.

In the present study, primary quartz was not found in thin sections of essentially fresh wall rock bordering the Radium Vein in the limited area sampled. The writer prefers to describe the rock here as a syenite, following Shand's classification, rather than a monzonite. Megascopically, it is a medium-grained, dark gray rock, having generally a nearly even-grained texture, and consisting essentially of orthoclase, plagioclase, pyroxene, and biotite. A small portion is porphyritic, with relatively large insets of augite.

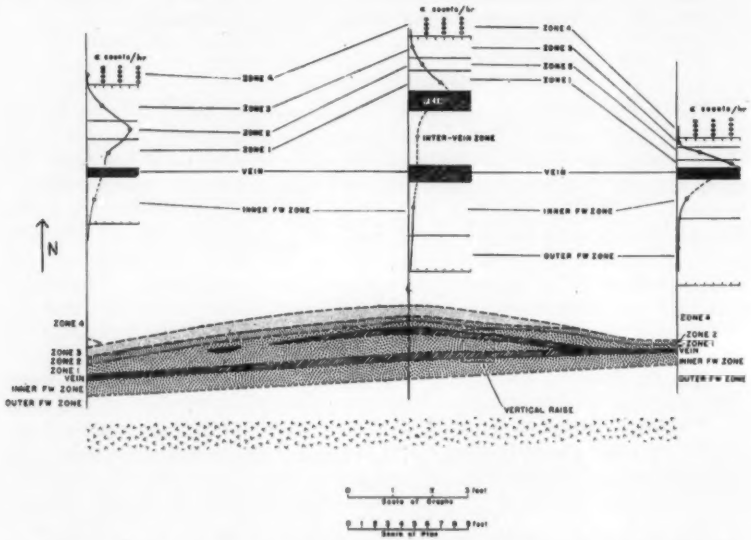


FIG. 1. Plan of a portion of the 1040 level, Caribou Mine, showing the relative alpha-activity of wall rock in the various alteration zones along the Radium Vein.

Microscopic study of the fresh rock shows that orthoclase and andesine constitute most of the rock, together averaging about 65 to 75 per cent. Orthoclase appears to be slightly more abundant than andesine, and is quite fresh. Some of the orthoclase is perthitic. The plagioclase crystals are lath-shaped and generally little altered, but some grains show incipient alteration to sericite, developed along cleavage planes in the host. Clay minerals are virtually absent in the fresh rock.

Mafic minerals represent about 20 to 25 percent of the total and include chiefly augite and biotite in about equal amounts; hornblende was found in one

thin section. Most crystals of augite are rather fresh, but some show development of biotite, chlorite, and a little epidote around the fringes. Biotite has been considerably corroded and marginally replaced by feldspar, and some has been altered to chlorite. Hornblende, rarely present, has been altered to biotite and chlorite along crystal boundaries.

Apatite and pyrite are abundant accessory minerals, and a small amount of sphene is present. Pyrite is developed interstitially and cuts feldspar grains, and euhedral crystals of apatite form abundant inclusions in the pyrite.

TABLE 1.

PARTIAL CHEMICAL ANALYSES[2] OF WALL ROCK SAMPLES ALONG RADIUM VEIN.

	K_2O	Na_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3 as analyzed	FeO	Loss 110° C
West Section									
Zone 4	5.55%	3.42%	3.70%	1.43%	54.25%	20.27%	4.26%	3.87%	1.38%
Zone 3	9.10	2.61	1.38	1.32	55.85	19.79	0.74	4.05	0.16
Zone 2	6.37	0.24	1.10	1.50	62.89	14.90	1.02	4.67	0.63
Zone 1	6.78	0.28	0.88	1.24	66.08	13.98	1.22	4.24	0.32
Inner FW Zone	10.22	0.70	1.33	1.77	51.66	20.54	2.87	6.08	0.29
Middle Section									
Zone 4	6.18%	3.31%	3.34%	1.24%	55.66%	19.89%	2.57%	3.10%	1.19%
Zone 3	8.67	2.39	1.77	1.12	55.86	20.38	2.07	3.40	0.28
Zone 2	5.76	0.60	2.40	1.79	53.10	20.60	4.93	2.13	4.51
Zone 1	10.26	0.82	1.65	1.09	57.63	20.47	1.13	2.83	0.34
Inter-vein Zone	9.35	0.40	0.94	1.28	60.28	17.79	1.10	3.96	0.32
Inner FW Zone	8.42	0.48	1.26	1.35	54.97	21.13	1.90	3.70	0.48
Outer FW Zone	5.44	3.30	3.60	1.33	54.14	20.36	3.57	3.79	1.21
East Section									
Zone 4	4.81%	3.10%	6.84%	3.11%	51.24%	19.69%	6.41%	2.88%	0.11%
Zone 2	3.21	0.68	2.37	3.53	48.04	19.11	6.73	3.71	6.61
Zone 1	8.60	0.47	1.28	2.57	46.04	18.81	2.76	8.83	0.45
Inner FW Zone	7.42	0.26	2.34	3.41	46.14	18.77	2.20	8.18	0.28
Outer FW Zone	4.83	3.55	6.43	2.60	52.24	20.05	5.86	2.51	0.16

These inclusions were apparently unaltered by pyrite, which formed by deposition and replacement along boundaries of the earlier minerals. Some fine-grained calcite is present in a few tiny veinlets as well as irregular masses replacing pyroxene; the calcite appears to be a result of hydrothermal activity associated with the formation of the adjacent vein.

The classification of the wall rock of the Radium Vein as a syenite is based on its leucocratic character, the predominance of orthoclase over plagioclase, and the identification of the plagioclase as andesine. Partial chemical

[2] Obtained through Dr. C. J. Rodden, New Brunswick Laboratory, Atomic Energy Commission.

analyses of essentially fresh syenite are represented by those headed "Zone 4" in Table 1.

Wall Rock Alteration.

The Radium Vein is enclosed by an envelope of markedly altered syenite about three to five feet wide. The altered rock consists of zones of different mineralogical composition that appear along the back of the drift as bands roughly parallel to the vein, marked by striking color and texture contrasts. Alteration is more strongly developed and extends farther from the vein on the north or hanging-wall side, where three distinct alteration bands may be seen. A fourth zone lying between these three and the fresh rock may be distinguished microscopically but differs from fresh rock in appearance only by a slight greenish coloration. Along the south wall only one zone is readily visible but a second zone adjacent to fresh rock may be distinguished microscopically.

The zones of alteration described in the following paragraphs are defined in terms of the well developed alteration pattern on the north (hanging-wall) side of the vein. The relations of the several zones are diagrammatically illustrated in Figure 1.

Adjacent to the vein, on the north side, is a zone of hard, compact rock, bleached nearly white. This zone varies from two to six inches in width, and is characterized by sericite and quartz. It will be called Zone No. 1. On the north side it is bounded abruptly by a second zone made up of a dark, gray-green, loosely coherent material that crumbles readily. The green color is caused by iron-stained montmorillonite, the most abundant alteration mineral in the zone. This zone has an average width of only two to three inches; it will be called Zone No. 2.

The next zone to the north is made up of a hard, compact, white rock closely similar in appearance and composition to Zone No. 1 but containing less quartz. Sericite is the most abundant alteration mineral and is accompanied by lesser amounts of montmorillonite and kaolinite. This zone, in contrast with the other alteration zones, is not continuous; in several places it lenses out completely. Its thickness varies from zero to about 12 inches. This zone will be referred to as No. 3.

Zone No. 3 marks the approximate outer limit of argillic alteration, and is separated from fresh syenite by a fourth zone of slightly altered rock that looks nearly fresh. In this rock the pyroxene is partly or completely altered to chlorite, calcite, and epidote. The zone is cut by fractures roughly parallel to the vein; the rock bordering the fractures is bleached white, and has the appearance of the rock in Zones No. 1 and No. 3. Zone No. 4 is not clearly demarcated; it grades into fresh monzonite, and its average thickness is not known.

The alteration zones on the south side of the vein are defined and described with respect to the zones along the north side. Bordering the vein on its south side is a band of hard, white, compact rock which is identical in appearance to Zones No. 1 and No. 3 on the north side. Microscopically it is found to contain the same kinds and about the same amounts of alteration

minerals as Zones No. 1 and No. 3, with sericite predominating, some kaolinite and a little montmorillonite, and abundant quartz in the portion near the vein (corresponding to Zone No. 1). This band of altered rock, which will be referred to as the "inner footwall zone," has a thickness of about 12 to 18 inches.

The "crumbly" altered rock of the No. 2 zone, characterized by abundant green, iron-stained montmorillonite, is entirely absent from the south side of the vein. Only very small amounts of this mineral were detected in the "inner footwall zone." The "inner footwall zone" is separated from fresh rock by a zone of slightly altered, green-tinged rock closely resembling fresh rock megascopically but containing small amounts of calcite, chlorite, and epidote. This zone corresponds to Zone No. 4 on the north side, and will be called the "outer footwall zone." As on the north side, this zone grades into fresh rock almost imperceptibly and its thickness is not known.

Laboratory Methods of Study.

Samples of each megascopically recognizable wall rock alteration zone taken along the three lines of section were studied. Identification of primary minerals was based on thin section studies. Identification of alteration products was based in part on thin section studies, and in part on x-ray diffraction, differential thermal analysis, and optical studies of fine-aggregate minerals concentrated by elutriation. Thin sections also yielded information on the textural relations of primary and alteration minerals, and the sequence of alteration.

A partial quantitative chemical analysis of each wall rock sample was made by Dr. C. J. Rodden at the Atomic Energy Commission Analytical Laboratory, New Brunswick, New Jersey. Na_2O, K_2O, CaO, MgO, SiO_2, Al_2O_3, FeO, Fe_2O_3, U_3O_8, and H_2O were determined for each sample submitted. In addition, semi-quantitative spectroscopic tests for Cu, Pb, Zn, Ti, and V were made on each sample. The analyses furnished data useful in evaluating the important chemical changes undergone by the syenite during alteration, and in correlating chemical changes in the rock with mineralogical changes determined by microscopic study, x-ray diffraction, and differential thermal analysis. In order to determine accurately the extent of uranium leakage from open fractures into wall rock during vein deposition, alpha-counts on all samples of fresh and altered wall rock were made by the author with the use of alpha-scintillation counting equipment at the Lamont Geological Observatory, Columbia University.

Alteration Minerals.

The alteration minerals identified are montmorillonite, kaolinite, sericite, chlorite, epidote, quartz, calcite, siderite, pyrite, and hematite. Montmorillonite, with $n_x = 1.509$ and $n_z = 1.541$, gave a thermal curve characteristic of the mineral (see Table 2), and x-ray patterns of the material agree with montmorillonite. Kaolinite, less abundant than montmorillonite, also gave a characteristic thermal curve (see Table 2), and thin section identification on

the basis of low birefringence, low relief, and aggregate structure was further verified by x-ray powder patterns.

Sericite, the most abundant fine-aggregate mineral, has $n_x = 1.555$ and $n_z = 1.593$. The x-ray pattern is similar to standard patterns, and the thermal curve showed no significant reactions. Identification of chlorite was based on its green color, micaceous form, very low birefringence, and an anomalous low first order blue interference color. The extremely low birefringence and anomalous interference color suggest penninite. Epidote, quartz, calcite, siderite, pyrite, and hematite (only a few scattered grains) were identified on the basis of diagnostic properties in thin section.

TABLE 2.

DIFFERENTIAL THERMAL AND X-RAY DATA ON ALTERATION MINERALS.[3]

Part A. Differential Thermal Analysis Data (Semi-quantitative).

	Montmorillonite (Endothermic peaks 175° C, 750° C, 920° C; exothermic peak 975° C)	Kaolinite (Endothermic peak 580° C, exothermic peak 1000° C)	Sericite (No thermal reaction detected)
Zone 3	15–25%	10–15%	—
Zone 2	40%	25–40%	—
Zone 1	10–15%	15–25%	—
Inter-vein Zone	Not detected	Not detected	—
Inner FW Zone	Not detected	25–40%	—

Part B. X-ray Data (Qualitative—Standards Not Available).

	Montmorillonite	Kaolinite	Sericite
Zone 3	Not detected	Weak	Strong
Zone 2	Strong	Moderate	Not detected
Zone 1	Not detected	Moderate	Moderate
Inter-vein Zone	Not detected	Not detected	Moderate
Inner FW Zone	Not detected	Moderate	Moderate

Mineralogical Description of Alteration Zones.

Zone No. 4.—As stated previously, Zone No. 4 is not sharply separable from fresh rock either megascopically or in thin section; most of the rock in this zone is essentially fresh. All of the primary minerals are present, including orthoclase, andesine, augite, hornblende (rare), biotite, apatite, sphene, and pyrite. Of these, only augite, hornblende, and biotite are appreciably altered.

Augite crystals were largely replaced by fine-grained calcite and pyrite, some chlorite, and a little epidote. Hornblende, rarely present, shows marginal alteration to biotite, and biotite is in part altered to chlorite interlaminated in places with pyrite. The close association of pyrite with chlorite is thought to represent the sulfidation of iron released in the alteration of augite and biotite to chlorite. A small amount of hematite occurs with the chlorite and primary mafic minerals. Although orthoclase remained prac-

[3] Based on analysis of elutriates of samples from middle sampling section.

tically fresh, plagioclase shows incipient alteration to sericite, montmorillonite, and kaolinite. A small amount of secondary quartz occurs in vugs and veinlets as clear, well formed crystals.

Zone No. 3.—The positions of former pyroxene crystals are marked by clots of calcite with a little epidote; almost no pyroxene remains. Biotite, almost completely altered, is represented chiefly by a mixture of muscovite and calcite in alternating, parallel laths. Chlorite has essentially disappeared.

Plagioclase and orthoclase show strong attack, having altered chiefly to sericite (estimated to comprise about 20% [4] of the rock), together with some montmorillonite and kaolinite. Each of the clays is estimated to be present in amounts of about five to eight percent, although the total and relative amounts of clay vary considerably over short distances. Orthoclase shows considerably less alteration than plagioclase, and montmorillonite is slightly more abundant than kaolinite in the feldspars. Sericite replaces feldspars in different ways: (1) as a boxwork of sheets largely aligned with cleavage directions in the host, (2) as fracture fillings of apparently random orientation, and (3) as replacement veinlets along mineral boundaries. Small isolated clots of both kaolinite and montmorillonite are engulfed and veined by sericite.

Calcite veinlets, some containing small amounts of galena and sphalerite, cut across all other minerals of the zone including clay and sericite. A few quartz veinlets also are present.

Zone No. 2.—Plagioclase has been completely altered and orthoclase is strongly attacked. The chief alteration product of the feldspars is green-stained montmorillonite, which forms numerous clots connected by a network of veinlets. Kaolinite is closely associated in pockets with montmorillonite, and is more abundant than in Zone No. 3. In contrast with the clays, sericite, abundant in Zone No. 3, is present in relatively small amount in Zone No. 2. The estimated amounts of the three minerals are: montmorillonite 35 percent, kaolinite 10 percent, sericite less than five percent.

Biotite, almost absent in Zone No. 3, is present in abundance, although displaying some alteration to sericite. Calcite and quartz veinlets cut all other minerals in the zone.

The green color of the montmorillonite appears to be due to a coating of material of an undetermined nature. A solution of this substance in 1:10 hydrochloric acid gave, with potassium ferricyanide and potassium ferrocyanide, a strong reaction for ferrous iron and a markedly weaker test for ferric iron. The ferrous compound responsible for the color has not been identified.

Zone No. 1.—Of the essential primary rock minerals, only biotite and orthoclase are found in Zone No. 1. Most of the original biotite has been completely altered to flakes of muscovite, which retain the crystallographic orientation of the host. Orthoclase is strongly attacked, going chiefly to sericite, but in some parts of the zone as much as half of the original orthoclase remains. In other portions of the zone, both orthoclase and biotite have been completely destroyed. Here only apatite represents the original rock minerals.

The mineralogy of Zone No. 1 is similar to that of Zone No. 3, but relative amounts of the minerals are somewhat different. Sericite is the most

[4] See discussion of quantitative estimation of alteration products below.

abundant of the fine-aggregate minerals in both zones, comprising about 25 percent of the rock in Zone No. 1. Montmorillonite, about 5 percent of the material of Zone No. 1, is slightly less abundant than in Zone No. 3, while kaolinite represents a larger amount of Zone No. 1, about 10 percent. The greatest difference between the zones is in the greater abundance of secondary quartz and calcite in Zone No. 1. Fractures filled with quartz, calcite, or siderite are numerous in Zone No. 1 and large amounts of fine-grained quartz have impregnated the strongly altered rock, especially the portion immediately adjacent to the vein. Here the rock is a fine-grained aggregate consisting of quartz, sericite, calcite, kaolinite, and a little montmorillonite, cut by veinlets of quartz, calcite, and siderite. The calcite veinlets show irregular, unmatched walls, and join irregular replacement bodies of calcite. Calcite veinlets are cut and in some cases displaced by quartz veinlets with clearly defined walls, and both types show a few crystals of sphalerite and galena in the central portion.

Outer Footwall Zone.—The outer of the two alteration zones in the footwall of the vein corresponds to Zone No. 4 in mineralogy and in its position adjacent to fresh rock. The rock of the outer footwall zone is indistinguishable megascopically from fresh rock. Only augite shows strong alteration, having altered largely to fine-grained calcite together with small amounts of chlorite and epidote. Some biotite flakes were marginally altered to chlorite, and the feldspars show incipient alteration to sericite and calcite. Calcite also appears in scattered veinlets.

Inner Footwall Zone.—The inner footwall zone, which includes all of the visibly altered rock, corresponds to Zone No. 1 in its position next to the vein, and is similar to Zones No. 1 and No. 3 in appearance and in the kinds and amounts of alteration minerals present. Augite and andesine are completely altered, augite largely to calcite, and andesine to sericite, kaolinite, a little montmorillonite, and calcite. In places biotite and orthoclase also are completely destroyed, but abundant remnants of orthoclase and some crystals of biotite are present in most of the zone. Biotite altered to sericite, and orthoclase chiefly to sericite and kaolinite.

Sericite is the most abundant fine-aggregate alteration mineral, comprising about 20 percent of this zone, but kaolinite (more abundant here than in any of the hanging-wall alteration zones) makes up about 15 percent of the rock. Montmorillonite is present only in minor amount, less than five percent. As in Zone No. 1, the strongly altered rock immediately adjacent to the vein has been impregnated abundantly with fine-grained quartz and calcite, and these minerals form rather numerous veinlets throughout the zone.

Inter-Vein Zone.—Along the central member of the three sections sampled, the Radium Vein is split into two veins about 18 inches apart, the northward of the two ending midway between the central and the west sampling section. The wall rock between the veins shows strong alteration and is similar in appearance and mineralogy to Zones No. 1 and No 3 on the hanging-wall side, and the inner footwall zone. Although scattered remnants of orthoclase and a few flakes of biotite are seen, augite and andesine have disappeared altogether. The alteration minerals are the same as in Zones No. 1 and No. 3.

Sericite is the most abundant, making up about 30 percent of the rock. Montmorillonite and kaolinite are present only in very minor amount, each of them less than five percent. The altered rock is abundantly impregnated and veined by fine-grained quartz and calcite.

Semi-Quantitative Estimation of Alteration Minerals.

In the above description, estimates of the amounts of alteration products in the various zones adjacent to the Radium Vein were based on microscopic examination of thin sections, and study of x-ray diffraction and differential thermal analysis patterns. These estimates indicate the general order of magnitude only; they are necessarily crude, for the following reasons:

(1) Accurate percentage determinations cannot be obtained from the thin sections. Kaolinite and montmorillonite are finely intermixed, and the clays in many cases are disseminated through sericite. The use of statistical counting techniques on this material was not feasible. Further, although kaolinite is in general clearly recognizable microscopically, sericite flakes oriented so as to show first order interference colors are not always distinguishable from shreds of montmorillonite, where the two are interspersed (especially in Zones No. 1 and No. 3).

(2) Differential thermal analysis, normally one of the best techniques for semi-quantitative clay mineral evaluation, is not adequate in the present problem because of the nature of the material. In several of the zones, either montmorillonite or kaolinite (or both) is present in amounts less than 10 percent, which is close to the limit of sensitivity of the method. It therefore was necessary to concentrate the fine-aggregate minerals by elutriation, and the portion of the total fine-aggregate minerals in the rock represented by the concentrate was not determinable. In addition, since montmorillonite and kaolinite are intimately mixed in all of the zones, pure fractions of each were not obtainable for the preparation of standards.

(3) X-ray evaluation was inhibited by the same factors affecting thermal analysis interpretations: a lack of pure mineral separates for pattern comparisons, and the necessity of analyzing concentrates rather than bulk samples. However, the patterns aided greatly in enabling at least a rough comparison of the clays with sericite, which is thermally inactive in the temperature range (to 1000° C) used.

While an accurate quantitative estimate was not obtained, a correlation of microscopic, x-ray, and differential thermal data has given a general picture of the relative importance of montmorillonite, kaolinite, and sericite in the different zones. The middle of the three sample sections (the most complete) was selected for this purpose. An average of five thin sections, representing different alteration intensities, was used for each alteration zone. The proportion of the total feldspars and biotite altered to montmorillonite, kaolinite, and sericite was estimated, and the results from thin sections in each zone averaged. The ratio of kaolinite to montmorillonite was estimated chiefly from the thermal curves, and checked by x-ray data. In turn, the ratio of sericite to each of the clays was estimated from the x-ray patterns. The

total of sericite, montmorillonite, and kaolinite was made equivalent to the total alteration material estimated from thin sections. X-ray and differential thermal patterns for elutriation concentrates from the east and west sample sections agreed well with the results obtained from the middle section. Within a given zone, however, considerable variation in the amount of each of the three fine-aggregate materials was found, depending on position within the zone, and probably also position with respect to fractures connecting with the vein. The figures given, therefore, represent estimated averages for zones. The x-ray diffraction and differential thermal data used for the semi-quantitative estimates are summarized in Table 2.

Alteration Types and Their Paragenesis.

Five main types of alteration have been recognized. Their sequence, determined by the textural relations of the alteration minerals and by the spatial distribution of the alteration zones, is as follows:

1. *Chlorite-calcite-epidote-pyrite* alteration of augite.
2. *Argillization:* alteration of orthoclase and andesine to montmorillonite and kaolinite.
3. *Sericitization:* alteration of orthoclase, andesine, and biotite to sericite.
4. *Carbonatization:* veining of earlier minerals and replacement of feldspars by calcite and siderite.
5. *Silicification:* veining of earlier minerals and replacement of already strongly altered rock adjacent to vein by fine-grained quartz.

The time position of the chlorite-calcite-epidote-pyrite alteration is evidenced by its spatial position (farthest from the vein) and by the relative freshness of the feldspars and biotite. The age relation between sericite and the clay minerals (kaolinite and montmorillonite) is not reflected by their zonal distribution. Although they are found in the same alteration zones, sericite and the clay minerals apparently did not form in the same portion of the altered rock at the same time. Sericite forms numerous veinlets cutting kaolinite and montmorillonite, and the clays are commonly engulfed by sericite. In all cases where the age relation between clays and sericite is clearly evidenced, sericite is later than the clays.

Calcite, siderite, and quartz are found in vugs and veinlets throughout the alteration envelope, but become progressively more abundant toward the vein. Their time relation to each other and to the other alteration minerals is indicated chiefly by abundant veining and cross-cutting relations. Deposition of the carbonates and quartz overlapped the third (sericitic) stage to a considerable degree, and may have been entirely contemporaneous with it.

The Anomalous Zone No. 3.

The sequence of altered zones observed at Butte, Montana by Sales and Meyer (24, p. 8–12) is composed of an outer zone characterized by chlorite, followed veinward by a zone of argillized rock with the ratio kaolinite: montmorillonite increasing veinward to the zone margin, and finally a zone of

sericitized rock adjacent to the vein. A similar sequence, lacking the chloritized zone, was described by Lovering (18) along the ferberite deposits of Boulder County, Colorado, a few miles east of Caribou. At Caribou this sequence, represented respectively by Zones No. 4, No. 2, and No. 1, is complicated by the presence of the strongly sericitized Zone No. 3. This zone is closely similar in its mineralogy to Zone No. 1, but the two sericitized zones are separated by the strongly argillized Zone No. 2.

Several features suggest that Zone No. 3 does not belong to the chronological sequence that might be indicated by the spatial arrangement of zones. It is believed, instead, that Zone No. 3 formed at the same time and by the action of the same vein solutions as did Zone No. 1. According to this hypothesis, the solutions responsible for the sericitization of Zone No. 1 were carried by fractures into Zones No. 2 and No. 3, and to a slight extent into No. 4. In Zone

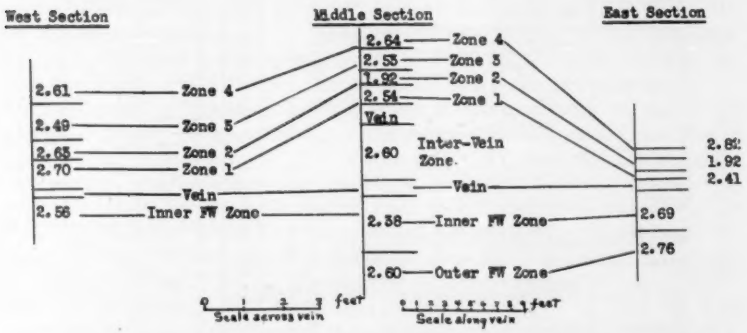
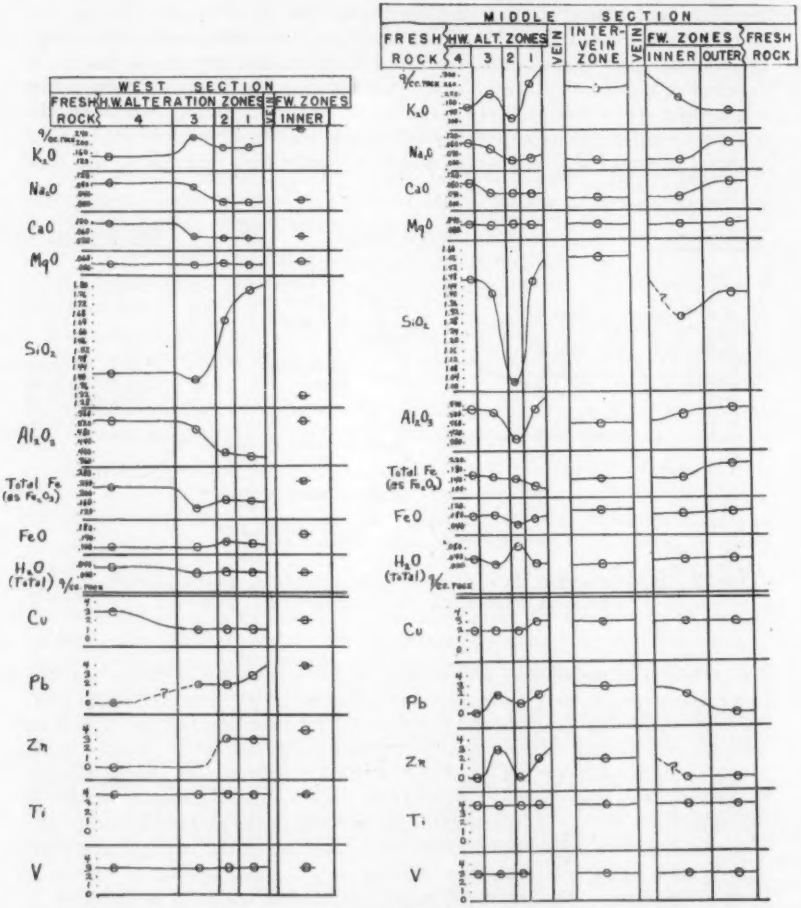


FIG. 2. Scale diagram showing variations in the bulk density of rock in the alteration zones along the Radium Vein, Caribou.

No. 3, which at the time of introduction of the sericitizing solutions was the outer, less strongly altered portion of the argillized zone (indicated by the presence of considerable kaolinite and montmorillonite, both of which are older than sericite), the solutions were free to permeate the moderately altered rock. Much of the remaining orthoclase and biotite were apparently altered directly to sericite, as in Zone No. 1. By contrast, only a minor amount of sericite is found in Zone No. 2. It is thought that swelling of the abundant montmorillonite in Zone No. 2 prevented thorough permeation of the strongly argillized rock by sericitizing solutions, thus allowing only a minor amount of sericite to form in this zone. The solutions, largely confined to fractures in Zone No. 2, passed on into Zone No. 3 and, to a limited extent, into Zone No. 4, where they were able to permeate the rock more completely and replace orthoclase and biotite with sericite as outlined above.

A factor favoring the hypothesis suggested is the evidence that sericite in

Zones No. 2 and No. 3 is later than the clays. Further evidence is seen in the more advanced alteration of biotite in Zone No. 3 than in Zone No. 2. The discontinuous character of Zone No. 3 also appears to harmonize with the suggested hypothesis. If Zone No. 3 had formed prior to Zone No. 2, there would have been no barrier such as the montmorillonite zone in the path of



FIGS. 3 AND 4. Diagrams showing variations in chemical composition of the different alteration zones along the Radium Vein, Caribou (West and Middle Sections). Analyses expressed in Arbitrary Units: 4 = 0.1 – 1.0%; 3 = 0.01 – 0.1%; 2 = 0.001 – 0.01%; 1 = less than 0.001%. Scale: One inch = Three and one-half feet.

the solutions responsible for Zone No. 3 alteration, and Zone No. 3 might be expected to be continuous, as are Zones No. 2 and No. 1. However, if Zone No. 3 formed subsequently to Zone No. 2, as is believed to be the case, the local absence of fractures across the montmorillonite-rich Zone No. 2 might prevent the passage of altering solutions through Zone No. 2, and Zone No. 3 would not be formed in such places. The presence in Zones No. 2, No. 3, and even in No. 4 of fairly numerous fractures filled with calcite and quartz indicates that, in many places, vein solutions were able to cross Zone No. 2. Some of these late fractures are lined with narrow bands of sericite.

If Zone No. 3 had formed earlier than Zone No. 2, it would seem necessary to assume that the altering solutions had changed their character through a complete cycle. After the formation of the sericite-rich Zone No. 3 and the very different, argillaceous Zone No. 2, the formation of another sericitic zone (No. 1) similar to No. 3 would require the solutions to change back to a composition similar to that responsible for Zone No. 3. The hypothesis of the by-passing of Zone No. 2 by the solutions that attacked Zone No. 1 and the simultaneous formation by these same solutions of a similar alteration mineralogy in Zone No. 3 is believed to offer a simpler, more plausible explanation than a cyclic change in the character of the altering solutions.

One feature of the alteration that is not in harmony with the above explanation should be mentioned. If the montmorillonite-rich Zone No. 2 formed prior to deposition of uraninite in the vein (evidence concerning the time relation of alteration to vein deposition was not found in the microscopic study), it is apparent from alpha-count data on distribution of uranium in the wall rock, discussed below, that uranium was nonetheless able to penetrate the argillized rock of this zone—although in very small amounts. However, spectroscopic analysis of the altered rock for lead and zinc (Figs. 3, 4, 5) shows smaller amounts of these metals in Zone No. 2 than in Zone No. 3 in two of the three sample sections. It is interesting that the third (west) section shows very little montmorillonite in Zone No. 2 (due apparently to the presence of a small offshoot from the main vein).

Variation in Chemical Constituents of Altered Wall Rock.

In order to enable direct evaluation of the changes in chemical constituents of the syenite that took place during alteration, the percentages found by quantitative analysis (Table 1) were multiplied by the bulk density of the rock sample (determined by the Russell tube method (23), using rock chips saturated in vacuum with tetrachlorethane). In Figure 2, the bulk densities of the various samples are plotted in their appropriate position with respect to the vein and alteration zones. In Figures 3, 4, and 5, the amounts of each element determined, expressed in grams per cubic centimeter of rock, are plotted in their appropriate positions with respect to the vein and alteration zone boundaries. Curves connecting the points along each line of section show an interpretation of general trends in the chemical alteration. The assumption of constant volume was made because of a lack of noticeable slumping, major fracturing, or displacement along fractures. The swelling of mont-

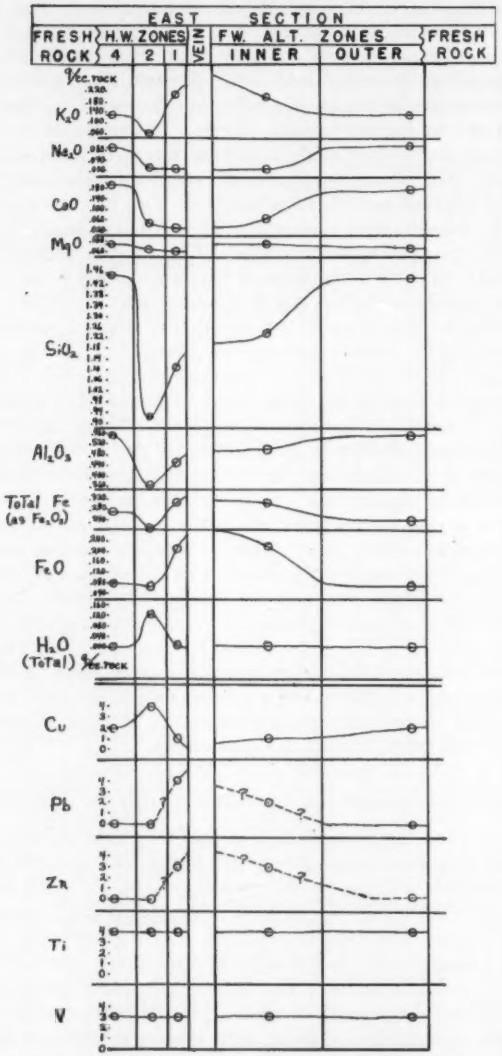


FIG. 5. Diagram showing variations in chemical composition of the different alteration zones along the Radium Vein, Caribou (East Section). Spectrographic analyses expressed in Arbitrary Units: 4 = 0.1 − 1.0%; 3 = 0.01 − 0.1%; 2 = 0.001 − 0.01%; 1 = less than 0.001%. Scale: One inch = One and one-half feet.

morillonite in Zone No. 2 apparently was made possible by the removal of a considerable portion of the original material, as indicated by the lowered bulk density.

The most consistent trends are shown by the curves for lime and soda. The three lines of section show a strong leaching of lime and soda beginning with Zone No. 4 and continuing veinward. Losses in lime were most rapid in Zones No. 4 and No. 3, as a result of the complete breakdown of pyroxene and strong attack on plagioclase. Soda likewise was most strongly leached in the outer zones, corresponding to the alteration of plagioclase. As pointed out by Sales and Meyer (24, p. 14), the removal of lime and soda across the altered rock apparently reflects the inability of these base and alkali metals to form stable compounds in the new environment.

Potash in all sections shows higher values adjacent to the vein than in fresh rock. The smallest amount in all three sections is in Zone No. 2, which contains little sericite. Zones No. 3 and No. 1 contain the largest amounts of potash, reflecting the abundance of sericite in these zones.

Magnesia remains nearly constant through the altered rock. Most of the magnesia freed during the alteration of pyroxene was apparently fixed in montmorillonite, and little escaped into the vein. The higher percentage of magnesia in the montmorillonite-rich Zone No. 2 is offset by the markedly lower bulk density of this rock, so that the gram weight of magnesia is about the same as in other zones.

Silica shows a less consistent trend than the base and alkali metals. On the hanging-wall side, it generally decreases toward the vein through Zone No. 2, then shows a strong increase in Zone No. 1 (in the west section, a strong increase across Zone No. 2 as well as No. 1). However, the amount of silica in Zone No. 1 may be greater or less than that present in fresh rock. On the footwall side, silica is less abundant in the inner zone than in the outer. The intensity of silicification of the rock adjacent to the vein varies considerably along the vein. In places silica from the breakdown of pyroxene, feldspars, and biotite apparently escaped into the vein instead of being redeposited along the margin.

Alumina generally is present in slightly smaller amount adjacent to the vein than in fresh rock, the smallest quantities being found in Zone No. 2. The curves for iron oxide show a tendency for ferrous oxide to remain nearly constant across altered rock in two sections while total iron decreases veinward. In the third section, ferrous oxide increases veinward, while total iron increases less rapidly. Ferric oxide decreases veinward in all three sections. Taken together, the curves indicate an increasingly reducing environment as the vein is approached, which accounts for the fairly abundant occurrence of pyrite in the altered rock, and hematite is present in extremely minor amount. The zone of hematitic alteration present in many of the Canadian uraninite deposits is lacking here, probably due at least in part to the reducing action of abundant sulfur in the mineralizing solutions.

Curves showing the distribution of copper, lead, zinc, titanium, and vanadium, based on semi-quantitative spectroscopic analysis, are reproduced in Figures 3, 4, and 5. As indicated by the curves, lead and zinc are present in

greatest amount adjacent to the vein, and in decreasing amount outward from the vein; neither was detected in fresh rock. This distribution will be compared below with alpha-count data on uranium.

The distribution of copper in the wall rock is erratic. Although one of the sections shows copper decreasing slightly in amount outward from the vein, the other two show percentages increasing with distance from the vein, and larger amounts in fresh syenite than in altered rock adjacent to the vein. Since chalcopyrite is an important vein constituent, leakage of copper into the wall rock might have been expected to give a distribution similar to that of uranium, lead, and zinc. The reason for the anomalous distribution is not known.

Comparison with Alteration Patterns Described from Other Localities.

The pattern of alteration described above has a number of features in common with alteration suites described from various localities. The major features of the pattern—relative stability of the primary mineral groups in zones of different alteration intensity, the alteration minerals developed, sequence of formation of the alteration products, and progressive chemical changes with increasing intensity of alteration—conform rather closely to a general pattern that has emerged from hydrothermal alteration studies in many districts. The Caribou alteration differs from others in certain details, as would be expected from the variability in composition of rocks affected, and in the ore-forming solutions responsible for the chemical and mineralogical changes.

The present study may most directly be compared with two recent hydrothermal alteration studies of vein deposits in monzonite and quartz monzonite country rocks: Lovering's (18) investigation of the Boulder County, Colorado tungsten mineralization, and Sales and Meyer's (24, p. 1–25) study of the alteration accompanying ore mineralization at Butte, Montana. Recent independent investigations by Kerr (12) and by Schwartz (25) of wall rock alteration associated with certain "porphyry copper" deposits of the Southwest are not as closely comparable because of the disseminated nature of the mineralization, and its much larger scale features, but the broad, overall alteration pattern at some of these is similar to that at Caribou.

Associated with the ferberite veins of Boulder County, Lovering found two characteristic envelopes of altered quartz monzonite. An outer zone, characterized by predominance of the clay minerals allophane, kaolinite, montmorillonite, beidellite, and hydrous mica over sericite, is separated from the vein by a casement of more intensely altered monzonite in which sericite and fine-grained quartz predominate over clays.

The argillized zone is subdivided into three subzones: (1) an outer subzone characterized by allophane, montmorillonite, hydrous mica, and some sericite; (2) a "transition" zone marked by abundant beidellite, and (3) an inner subzone characterized by abundant dickite with lesser montmorillonite and beidellite. In the argillized zone, quartz and orthoclase are essentially stable, and biotite is relatively stable but shows development of sericite in

the most intensely altered portion. Oligoclase and andesine are the most susceptible to alteration, showing moderate to strong development of clays together with some sericite. This zone corresponds to "Zone 2" of the Caribou alteration, but shows a wider variety of clay minerals than does the Caribou argillized zone. The districts are similar in the strong development of montmorillonite-group clays in the outer part of the argillized rock, with an increasing ratio of kaolinite group to montmorillonite group clays as the vein is approached. This feature is in accord with the Butte alteration pattern. The stability of biotite in the argillized zone of the Boulder ferberite veins and Butte is matched by the behavior of biotite in this zone at Caribou. However, the early development of chlorite from biotite, characterizing "Zone 4" at Caribou and the outermost, slightly altered rock at Butte, is lacking in Lovering's sequence.

In the inner, sericitized zone adjoining the ferberite veins, allophane, dickite, and hydrous mica (the only remaining clays) show strong replacement by sericite and fine-grained quartz, the dominant alteration products. Biotite and orthoclase show strong replacement by sericite, which also replaced primary quartz to some extent. The evidence indicates that fine-grained quartz deposition and replacement overlapped and followed sericite formation, and that both are predominantly later than the clays. "Zone 1" at Caribou closely parallels the innermost of Lovering's zones, with strong development of fine-grained quartz and sericite, which replace the earlier clays and much of the remaining biotite and orthoclase.

The general arrangement of alteration products at Butte (24, p. 8–12) is similar to Lovering's alteration zones, and forms an even closer parallel to the Caribou pattern. Like Lovering, Sales and Meyer found an outer, argillized zone characteristically bounded veinward by a sericitized zone. The argillized zone is subdivided into an outer "montmorillonite subzone" and an inner "kaolinite subzone." At the outer edge of the altered rock, biotite is partially replaced by chlorite, and hornblende by chlorite, calcite and epidote. This portion of the altered rock corresponds to "Zone 4" at Caribou, and, as noted above, has no counterpart in Lovering's sequence.

Plagioclase at Butte was less stable than orthoclase, with considerable development of montmorillonite in plagioclase in the outer "montmorillonite subzone" while orthoclase remains nearly fresh. In the more intensely altered "kaolinite subzone," however, orthoclase was altered directly to kaolinite. The increasing kaolinite: montmorillonite ratio veinward across the argillized zone accords with Lovering's Boulder County sequence. The sericitized zone, adjacent to the vein, shows chiefly sericite, fine-grained quartz, and pyrite, and the primary silicates remaining unaltered in the argillized zone (chiefly orthoclase and biotite) were completely destroyed in the innermost zone.

The chief difference in the Caribou alteration pattern (aside from the anomalous "Zone 3," previously discussed) as compared with Sales and Meyer's zones is in the presence of considerable sericite outside the innermost zone, and of clays (especially kaolinite) in the inner, sericitized zone. In this respect, the Caribou alteration pattern is more nearly like the alteration along

the nearby ferberite veins. Also, in no thin section of even the most intensely altered Caribou material was complete destruction of the silicates noted.

The alteration of the Santa Rita stock in New Mexico by solutions accompanying copper mineralization (chiefly) has been the subject of a recent detailed study by Kerr (12) and co-workers. Although much of the ore mineralization was more or less disseminated, resulting in irregular shaped bodies, many of the broad features of the alteration mineralogy are similar to those of the small-scale, regularly outlined pattern at Caribou. Four stages, mappable as essentially separate field units, were recognized in the progressive alteration of the biotite granodiorite porphyry.

In Stage 1 (comprising "comparatively unaltered" rock) the ferromagnesian minerals, biotite and hornblende, were in part altered to chlorite, magnetite, and pyrite, while the felsic minerals remained essentially fresh. In Stage 2, chlorite replacement of biotite was important, but the chlorite disappeared in the more intensive Stages 3 and 4 (as it did also in Sales and Meyer's (24, p. 9) argillized and sericitized zones). Minor sericite replacement of biotite, and kaolinite development in feldspars, occurred in the more intensively altered portion of Stage 2. Stage 3 is characterized by the development of clays, especially hydromica (replacing biotite), and kaolinite and montmorillonite (chiefly in feldspars), together with some sericite. The ratio kaolinite: montmorillonite increases with the intensity of alteration approaching Stage 4. Some kaolinite remains in Stage 4 (the most intense), but is subordinate to sericite and fine-grained quartz, the most abundant alteration products. The overall pattern at Santa Rita of chloritic alteration followed successively by argillic and sericitic-silicic stages bears a close resemblance to the Butte and (excepting the chloritic phase) the Boulder County ferberite vein sequences, and to the pattern at Caribou.

In his study of hydrothermal alteration associated with a number of "porphyry copper" deposits in the Southwest, Schwartz (25) found a variety of alteration types. No district furnishes a simple example of one type, but each usually shows one type predominant over the others present. Four types in particular are discussed:

(1) Quartz-orthoclase alteration, found at Ajo, Ely, Bingham, and others.
(2) Quartz-sericite-pyrite alteration, exemplified by the Inspiration-Miami, Ray, and Sacramento Hill camps (among others).
(3) Sericitic and argillic alteration, with subordinate quartz, as at Morenci, Chino, Castle Dome, etc.
(4) Biotitic alteration, as at Bingham and Ely.

The third type, seritic and argillic alteration with subordinate quartz, is the only one embracing most of the main features of the alteration type found at Caribou in the present study. Schwartz (25, p. 321) found the argillic minerals in general earlier than sericite and quartz, in accord with the other localities described above.

The chemical changes during alteration show rather wide variation, as found by Schwartz (26) in a comprehensive review of alteration studies. However, by separating the individual examples on the basis of wall rock

type into basic (less than 52% SiO_2), intermediate (52–66% SiO_2), and acid (more than 66% SiO_2) groups, he found that "the most consistent changes are indicated by rocks of intermediate composition altered in the mesothermal zone. Silica and alumina show relatively small changes, and ferric and ferrous oxide, magnesia, lime, and soda with rare exceptions show a decided loss. Potash, iron sulfide, and combined water usually show large relative gains (26, p. 232–3)."

At Butte, Sales and Meyer (24) found strong decreases in lime, soda, and silica, with little change in potash and alumina, and a slight decrease in magnesia across the argillized zone. Continuing veinward across the sericitized zone, potash and silica show strong increases while the original trends of the other constituents remain essentially the same. These trends are similar to those found by Lovering with the Boulder County tungsten mineralization. The chief contributions to the wall rock found by Sales and Meyer were potash, sulfur, and water of hydration. Chemical changes accompanying wall rock alteration at Caribou (summarized previously) are similar to those described, but with silica much less consistent, and magnesia showing a strong percentage (but small absolute) increase in the montmorillonite-rich Zone 2. Of the chemical substances in the Caribou rock determined, only potash shows a consistent gain. Although sulfur and carbon dioxide were not determined, addition of these must have taken place, as indicated by abundant pyrite, calcite, and siderite. It seems probable that the potash contributed by the vein solutions had been leached from the wall rock traversed in the deeper portion of the stock.

Although similar in nature, the chemical changes reported by Lovering and by Sales and Meyer are interpreted differently in regard to the evidence they show concerning the nature of the vein solutions responsible. Lovering, largely on the evidence of pH conditions influencing natural formation and artificial synthesis of the clays and sericite, hypothesized a gradual change in character of the ore-forming solutions from acidic to basic. On the other hand, Sales and Meyer (using somewhat different experimental data on conditions favoring clay mineral formation) hypothesized simultaneous sericitization and argillization at different distances from the vein, with the vein solutions unchanging with time in their capacity to alter the wall rock.

Distribution of Uranium in the Wall Rock.

In order to determine the extent of uranium leakage from the vein into the surrounding wall rock, and the control imposed by wall rock alteration over the migration of uranium, alpha-counts of wall rock samples were made by the author using the thick source scintillation technique and equipment developed at the Lamont Geological Observatory (9) of Columbia University. Each sample was crushed to minus 20 mesh, and prepared as a "thick source" in a circular brass sample tray having an area of about 120 square centimeters. In the sample housing, this tray rests directly beneath the phosphor-coated base of a lucite cone, the upper end of which is in contact with the base of a photomultiplier tube. Alpha particles striking the silver-activated

zinc sulfide phosphor cause emission of photons of light, some of which are collected by the lucite cone and transmitted to the photo-multiplier tube. The resulting electrical impulses are amplified by a preamplifier attached to the top of the housing unit, and from there pass through a linear amplifier and a scaler to the recorder.

The counts obtained show the relative alpha-activity of the different wall rock samples but cannot accurately be translated to percent uranium. Splits of the material used for alpha-counts were analyzed quantitatively for uranium by Dr. C. J. Rodden, of the Atomic Energy Commission, New Brunswick Laboratory. These analyses give an approximate quantitative picture of the amount of uranium disseminated from the vein into the wall rock, but as an indication of the relative amounts of uranium in the various wall rock zones

TABLE 3.

DATA ON DISTRIBUTION OF URANIUM IN WALL ROCK ALONG RADIUM VEIN.

	% U by chemical analysis[5]	Alpha counts per hour (thick source, sample area 121.3 cm²)
	West Section	
Zone 4	0.0005%	145
Zone 3	0.0014	1880
Zone 2	0.0085	5023
Zone 1	0.0042	2661
Inner FW Zone	0.0012	738
	Middle Section	
Zone 4	0.0006%	172
Zone 3	0.0008	367
Zone 2	0.0062	1635
Zone 1	0.0021	3517
Inter-vein Zone	0.0032	1046
Inner FW Zone	0.0011	454
Outer FW Zone	0.0014	285
	East Section	
Zone 4	0.0004%	94
Zone 2	0.0025	2769
Zone 1	0.0097	4583
Inner FW Zone	0.0013	680
Outer FW Zone	0.0004	70

they are less accurate than the alpha-counts due to the difficulties encountered in the chemical determination of uranium in extremely low concentration. The chemical uranium determinations and the alpha-count data are shown in Table 3.

Figure 1 shows the alpha-counts plotted to scale with respect to the vein and alteration zone boundaries. The curves show a rapid decrease in counts with increasing distance from the vein, levelling off as fresh rock is approached. The one exception is found on the hanging-wall side along the west sampling section (Fig. 1), where the counts on Zone No. 2 material are higher than those for Zone No. 1. This anomaly is believed to be due to the intersection with Zone No. 2 (previously mentioned) of an apparently barren fracture

[5] Chemical Analyses by Dr. C. J. Rodden, U. S. Atomic Energy Commission, New Brunswick Laboratory.

which is an extension westward of the more northerly of the two veins sampled along the middle section. Zone No. 2 along this section also does not conform in alteration mineralogy with Zone No. 2 samples along the other sections.

The observed distribution could be explained by migration from the vein either of uranium during its deposition in the vein, or of radon accumulated since formation of the vein. The counts obtained are of the right order of magnitude to correspond to the chemical uranium determinations, as indicated by semi-quantitative calculations of equivalent uranium made with the alpha-counts by calibration with a strip of metallic uranium. However, the chemical uranium analyses, while showing the same trend as the alpha-counts, are not in the same proportions. This discrepancy may be due to the presence in the wall rock of more radon than that in equilibrium with uranium, together with an inconstant radon : uranium ratio; or it may be due to the lack of precision in chemical analysis of uranium in low concentration. The author believes that the latter factor is the more important and that the alpha-activity is due predominantly to uranium and the daughter products in equilibrium with it.

In fresh rock immediately outside the alteration envelope, the counts indicate a uranium percentage which is about normal for igneous rocks.[6] The outermost alteration zone gives somewhat higher counts than those for fresh rock. Thus uranium leakage apparently extended approximately to the outer limit of wall rock alteration on both sides of the vein. Higher counts obtained along the hanging-wall apparently correspond to the more intense alteration on this side of the vein, and, together with the coincidence of the outer limit of uranium addition with the outer limit of wall rock alteration, suggest considerable control by the wall rock alteration over the leakage of uranium. Further evidence for this is found in the regularity of uranium distribution, with consistently strong decreases in uranium content outward from the vein. If the uranium had moved mainly along fractures, not only should the outer limit of alteration place no restriction on uranium penetration; the uranium would also be expected to show a somewhat erratic distribution, according to the relative abundance of fractures in the different zones sampled. The observed pattern appears to favor diffuse permeation of porous altered wall rock as the dominant mode of uranium leakage.

Spectroscopic data on the distribution of lead and zinc in the wall rock (Figs. 3, 4, 5) provide an interesting parallel to the distribution of uranium. Like uranium, lead and zinc decrease with distance outward from the vein, but did not penetrate as far into the wall rock as uranium. The outer limit of both lead and zinc in the hanging-wall along the three sections is in Zone No. 2 or No. 3. Neither is present in even trace amount in fresh rock.

The reason for the greater penetration of wall rock by uranium than by lead and zinc does not appear to be due to differences in solubility, since lead and zinc have been carried about the same distance in spite of the marked difference in their solubilities. Although ionic diffusion appears to be the most probable manner of movement of the uranium (as well as lead, zinc and

[6] Holland, H. D., personal communication.

sulfur) through porous wall rock, the pattern of penetration by uranium, lead and zinc might appear to argue against this.

The factors controlling the rate of diffusion of metallic ions through semi-permeable membranes—or "impounding structures" in geological examples—have been considered by Mackay (19), based largely on the work of Freundlich (8). Where diffusion of molecular substances is concerned, these factors include (19, p. 17) (1) effective size of pores (actual size as modified by adsorption effects) and (2) properties of the substance: molecular size, degree of ionization, the rate of penetration which is a factor of hydrophilic strength (molecular or ionic affinity for water), and valency, which affects hydrophilic strength. It seems probable that the uranium, lead, and zinc in the Caribou wall rock were transported as ions, although whether simple or complex is not known. If complex ions were involved, their dissociation would correspond to the ionization of molecules, so that treatment of the metals as "ions" without knowing the kinds involved may over-simplify the picture.

Mackay derived a hydrophilic series (19, p. 22) from valence and from molecular and ionic size considerations (the affinity for water increasing with higher valence and smaller size), which was found to correspond to the general order of metal zoning in ore deposits: mercury, lead, zinc, copper, tin (from greatest to least penetrability). Tin was placed at the least penetrable end because of its high valence.

From Mackay's reasoning, uranium (with 4 + and 6 + as the common ions) might thus be expected not to penetrate as far as lead and zinc, which according to Mackay are closely similar in their diffusion rates. Thus transportation by ionic diffusion, by itself, would not account for the observed uranium-lead-zinc distribution. However, evidence concerning the paragenesis of the vein filling, discussed in detail below, indicates that the lead and much of the zinc had been deposited in an earlier stage of mineralization than uranium. It seems probable that the alteration envelope continued to expand outward after lead-zinc and prior to uranium deposition. There would thus have been a greater thickness of porous rock favorable to penetration available to uranium than had been available to the earlier lead and zinc. The possibility that the alpha-counts in the outer alteration zones are due to an excess of radon and not simply to uranium cannot be disproved, but the comparison of uranium distribution as indicated by chemical analysis and by alpha-counts is believed to support the predominance of uranium over excess radon in the altered rock.

MINERALOGY OF THE RADIUM VEIN.

Methods of Study.

Identification of the ore minerals of the Radium Vein was based chiefly on studies of polished sections with the reflecting microscope. Where identifications based on physical properties and etch tests were not conclusive, x-ray diffraction powder patterns were made on material gouged from polished sections or from hand specimens. Final identification of uraninite, proustite, and gersdorffite was based upon x-ray analysis. X-ray identification of gersdorffite was confirmed by qualitative microchemical tests for nickel, iron,

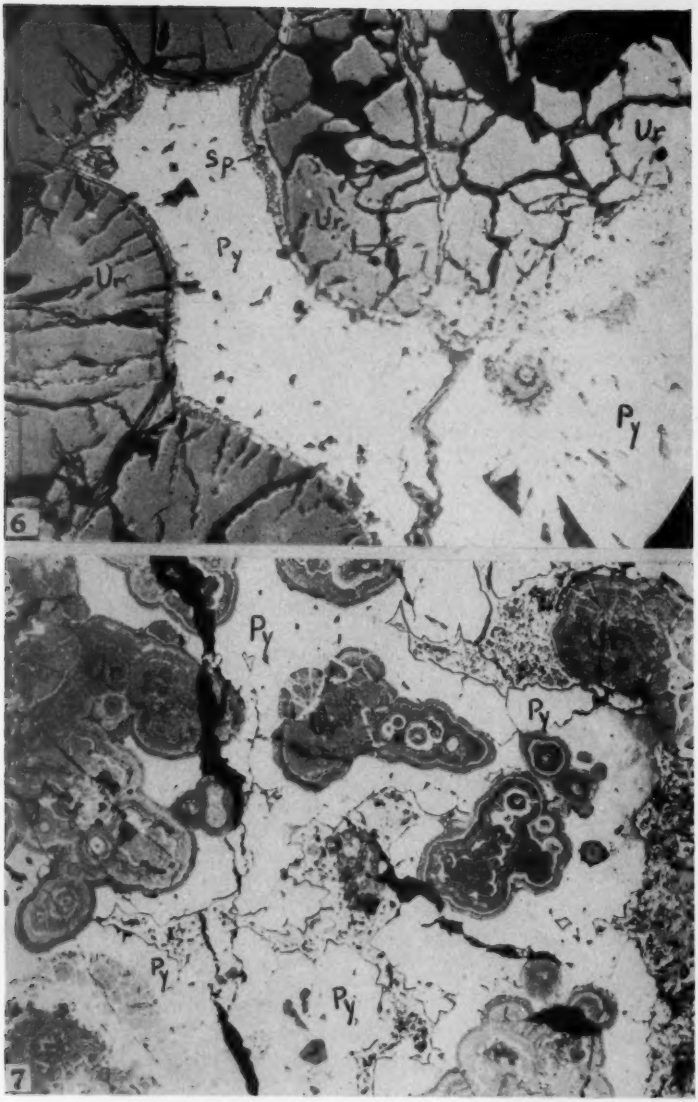


FIG. 6. Typical botryoidal structure and radially arranged fracture shown by uraninite (Ur), with portion of vug filling of later pyrite (Py). × 125.

FIG. 7. Pyrite (Py) banded concentrically about colloform uraninite (Ur). Some pyrite (Py) also interbanded concentrically with uraninite, or filling fractures in uraninite. × 100.

and arsenic. Identification of gangue minerals was aided by study of thin sections of the ores with the petrographic microscope. Sections used for this purpose were paired with polished sections cut along closely neighboring planes.

The polished section studies also yielded data on the texture and certain physical properties of the uraninite, and its spatial and paragenetic relations to other vein minerals. Thin sections of the ore aided in the study of relations of the ore minerals to the gangue and wall rock minerals.

General Statement.

The polished section studies revealed the presence of uraninite, pyrite, chalcopyrite, sphalerite, galena, gersdorffite, argentite, proustite, and native silver, associated with a gangue composed of quartz, chalcedony, calcite, siderite, and barite. These minerals are spatially arranged in two characteristic assemblages, which appear to represent different stages in the vein formation. In Stage A (the earlier), quartz, calcite, siderite, sphalerite, galena, and a little chalcopyrite were deposited. A small amount of pyrite probably belongs to this stage, but its relation to the other minerals is not clear. Uraninite was deposited early in Stage B. The other minerals of this stage are chalcedony, gersdorffite, chalcopyrite, sphalerite, pyrite, argentite, proustite, and native silver.

As may be seen from the photomicrographs (Figs. 6–24) the textural relations of the ore minerals are complex and varied, but in general consistent with regard to the evidence they show concerning age relations. A very fine, intricate, "eutectoid" texture involving uraninite, sphalerite, and silver minerals is especially abundant. It appears to represent replacement phenomena and neither supports nor invalidates the interpreted sequence based on other relationships.

Uraninite.

Two types of uraninite are present in the Caribou ore. One of these is a rather hard, dense, black material with pitchy luster, usually exhibiting a characteristic network of fractures. In much of the mineral, these are arranged radially and tangentially about the center of curvature of the botryoidal outline, and in many cases are filled with pyrite (Figs. 6, 8, 12). This type shows varying degrees of luster and hardness (all of it can be scratched with a steel needle), but generally displays the colloform texture that characterizes the material described from other localities, as Great Bear Lake (13), Joachimsthal (31), and Katanga (29). This structure is illustrated by Figures 14–17.

The other type of uraninite at Caribou is a soft, dull-lustered, black, fine-grained, porous, sooty material that fills fractures and coats open vugs in uraninite and sulfides. It does not show up well in microscopic examination of polished sections. In places the sooty material appears to grade into the lustrous variety of uraninite. The occurrence of the fine-grained, porous uraninite in fractures cutting most of the ore minerals indicates that it was deposited later than the lustrous, colloform material. It seems probable that

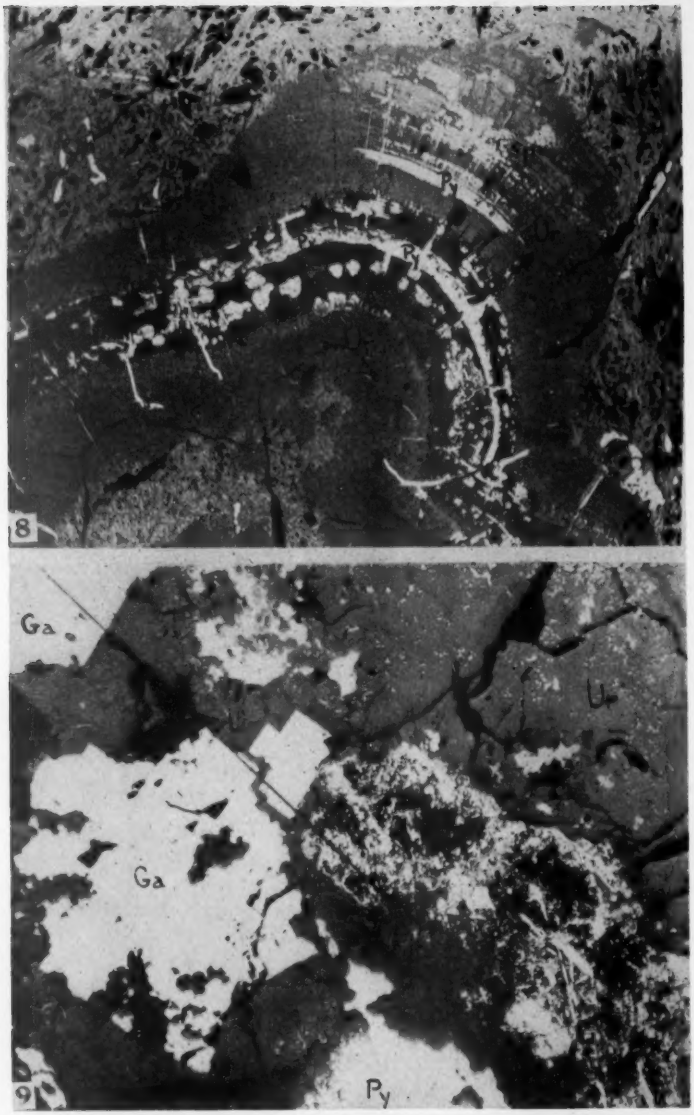


FIG. 8. Pyrite (Py) filling radial fractures in uraninite (Ur) and, with sphalerite (Sp), replacing uraninite along tangentially and radially arranged fractures. × 100.

FIG. 9. Galena (Ga) enclosed and cut by uraninite along cleavage fractures. Pyrite (Py) appears to have replaced uraninite. × 130.

it represents a reconstitution and redeposition of the earlier colloform uraninite, since uranium oxide is readily taken into solution. Some later uraninite showing the well defined colloform outlines of the more abundant first-formed material demonstrates the reworking activities of the vein solutions (Figs. 20, 23). However, in the case of the sooty uraninite the reworking may have been accomplished by circulating ground water rather than by late hydrothermal activity.

Paragenesis of the Vein Filling.

In the interpretation of paragenesis two main lines of evidence were considered: (1) sequence of mineral deposition in open fractures and cavities, and (2) truncation of earlier by later structures. In some cases replacement textures support interpretations based upon other relations, but were not in themselves considered as conclusive evidence of age relations.

Two relationships in particular suggest that the mineralization of Stage A preceded the Stage B sequence:

(1) Fragments of sphalerite and galena up to a half-inch in width, apparently belonging to an earlier mineralization period (Stage A), form inclusions within chalcedony and uraninite. Some sphalerite-galena fragments are coated by colloform uraninite.

(2) Although galena apparently was not crystallized in Stage B mineralization, it appears embedded in uraninite as isolated crystals with irregular rectangular outlines which are suggestive of cleavage fragments rather than whole crystals. Some of the galena grains have been fractured along cleavage directions and the fractures filled with uraninite. These relations are illustrated in Figures 9 and 10. Both cleavage outlines and fracture fillings show that galena is earlier than uraninite. The fragmental nature of the galena, indicative of a period of brecciation preceding uraninite deposition, and the position of uraninite at the beginning of Stage B mineralization indicate that galena was formed in an earlier stage of deposition.

Stage A.—The syenite wall rock had been strongly altered before the beginning of vein deposition. Cavities and fractures in the altered rock are lined with quartz, calcite, and siderite showing comb structure. Quartz coats bands of siderite and cuts siderite and calcite; but in places quartz is replaced by calcite, and euhedral crystals of quartz are engulfed by calcite. Quartz and the carbonates thus appear to have been introduced about contemporaneously, and to a large extent prior to metallic mineral deposition.

In general the deposition of a band of well formed quartz crystals immediately preceded the formation of sphalerite and galena, which occur chiefly as discontinuous, lens-shaped bodies rather than continuous vein fillings. Sphalerite is cut in places by quartz veinlets, but quartz deposition had practically ceased when galena crystallization began. Both sphalerite and quartz are traversed by veinlets of galena. In a few places, sphalerite and galena were preceded by a thin band of chalcopyrite lining the walls of veinlets; however, chalcopyrite is a minor product of Stage A deposition. Some pyrite that preceded Stage B mineralization may have formed during Stage A (Figs.

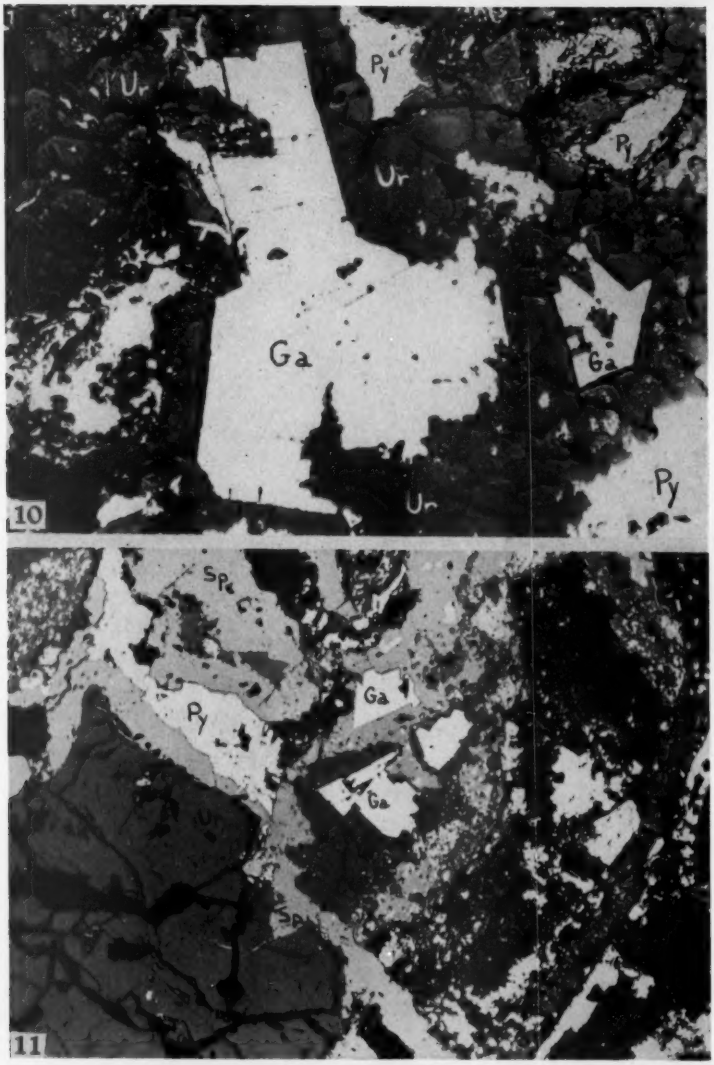


FIG. 10. Euhedral galena (Ga) crystals enclosed and partially replaced by uraninite (Ur). Pyrite replacing uraninite. × 110.

FIG. 11. Sphalerite (Sp) cutting and replacing uraninite (Ur). Galena (Ga) of Stage A engulfed by uraninite. Sphalerite replacement of uraninite appears to have stopped at boundary of one included galena crystal. × 100.

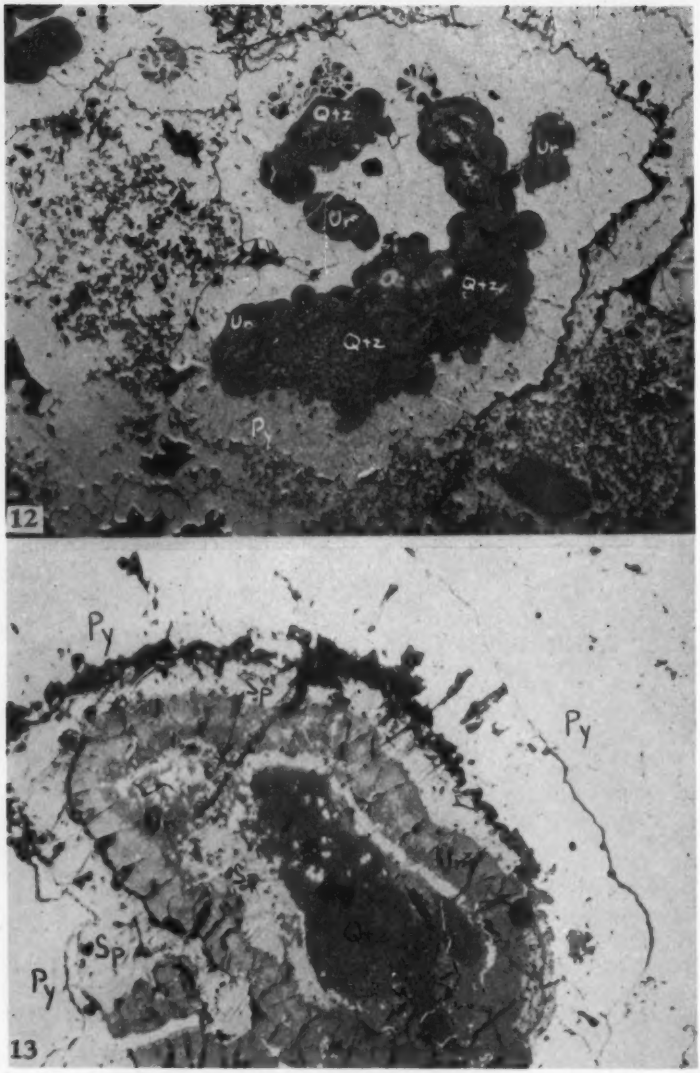


FIG. 12. Colloform uraninite (Ur) coating fragments of quartz (Qtz). Pyrite (Py) concentrically bands botryoidal uraninite and pyrite veinlets cut and replace uraninite. × 100.

FIG. 13. Uraninite (Ur), sphalerite (Sp), and pyrite (Py) successively deposited around quartz (Qtz); uraninite partially replaced by sphalerite. × 95.

16, 17), but pyrite closely associated with Stage A sphalerite and galena was not observed.

Stage B.—The presence of broken fragments of Stage A sphalerite and galena in Stage B uraninite and chalcedony indicates that a period of brecciation preceded the deposition of Stage B minerals. Vein filling in Stage B began with chalcedony, colloform uraninite, and gersdorffite. The uraninite in general forms a coating on chalcedony (Figs. 14, 15) or quartz (Figs. 12, 13), and replaced these to a slight extent. As illustrated in Figures 14 and 15, colloform banding of the uraninite does not conform to earlier chalcedony. Scattered small, irregular grains of gersdorffite occur in the uraninite. Gersdorffite apparently preceded uraninite in the sequence, as indicated by fairly numerous small veinlets of uraninite cutting gersdorffite. Veinlets with pyrite in the central position and uraninite along the margins also cut gersdorffite.

A little pyrite was deposited in the early part of Stage B; in places it is interbanded thinly with chalcedony (Figs. 14, 15) or uraninite, conforming to the botryoidal structure. Some pyrite that forms brecciated fragments in chalcedony or remnants in partial pseudomorphs of uraninite after pyrite is earlier than Stage B mineralization, but its relation to the sphalerite and galena of Stage A is not known. Pyrite partially replaced by uraninite is shown in Figures 16 and 17.

In general, the colloform uraninite is followed by a conformable band of sphalerite that cuts and extensively replaces the uraninite irregularly or along bands conforming to the botryoidal outline (Figs. 18–21). In places the uraninite is separated from the succeeding sphalerite by a very thin ribbon of pyrite or chalcopyrite. The inner boundary of the sphalerite layer maintains the botryoidal form of the uraninite and in many places the sphalerite band shows crystal terminations penetrating the succeeding botryoidal pyrite band.

In a few places, tiny botryoids of later uraninite coat sphalerite that had been deposited on more coarsely botryoidal uraninite belonging to the main period of uraninite deposition. The later uraninite occurs very sparingly and is believed to represent earlier uraninite which had been redissolved by the ore-forming solutions and precipitated somewhat later in the sequence, rather than a second introduction of uranium. This relationship is illustrated in Figure 20.

Chalcopyrite occupies a variable position in this sequence of deposition. Rarely it forms bands similar to the other minerals described, generally in uraninite or separating uraninite from succeeding sphalerite. More often it appears as tiny blebs in sphalerite. This feature has been attributed by Ridland (21) to exsolution. In places it also forms small veinlets in uraninite and quartz. Some chalcopyrite was deposited late in the vein or vug sequence, associated with argentite and proustite.

Pyrite follows sphalerite in the sequence and maintains the form inherited from the colloform uraninite (Figs. 7, 13, 20). This represents the most abundant pyrite deposition in the vein history. Prior to the introduction of this pyrite there appears to have been a considerable amount of brecciation of the earlier formed minerals, evidenced by numerous broken fragments of sphalerite and uraninite (Fig. 21) surrounded by pyrite. Some vugs show

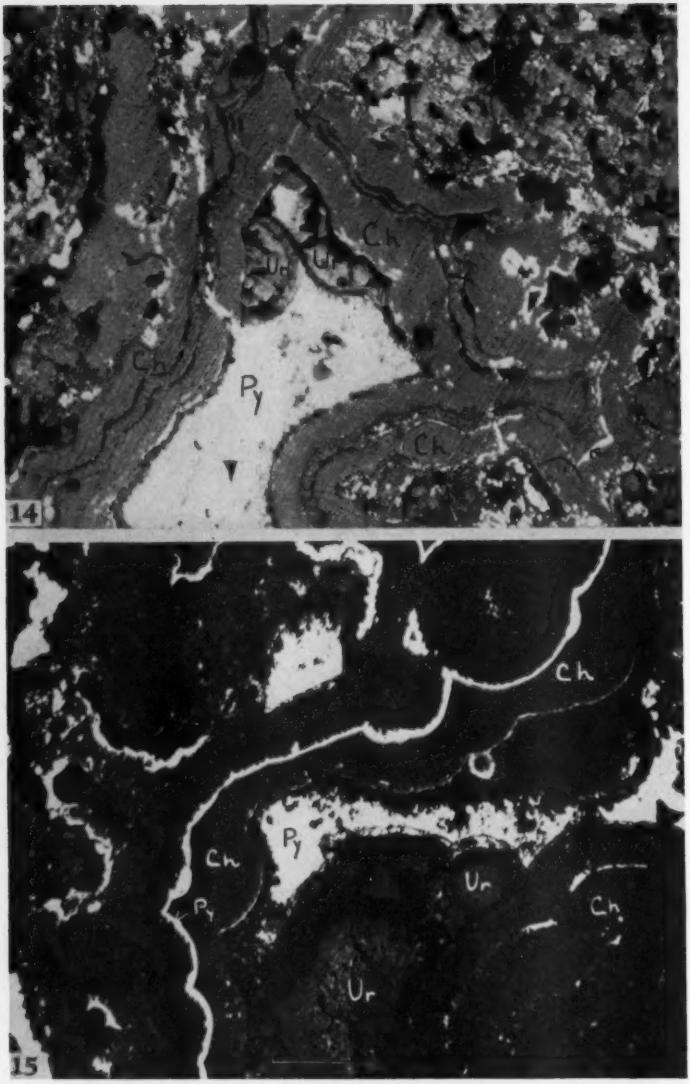


FIG. 14. Botryoidal uraninite (Ur) coating chalcedony (Ch); vug filling completed with pyrite (Py). × 100.

FIG. 15. Pyrite (Py) interbanded with colloform chalcedony (Ch); chalcedony coated by botryoidal uraninite (Ur), with pyrite completing vug filling. × 100.

no evidence of this disturbance, but instead an apparently uninterrupted Stage B sequence.

Fine, dark lines of an unidentified impurity within the pyrite conform to the outlines of the botryoidal banding and in places delineate crystal outlines facing the interior of the vein or vug. Besides the banded vug linings, pyrite occurs in numerous veinlets (Fig. 22) cutting uraninite, sphalerite, and quartz.

Although pyrite completes the filling in many vugs, in others it is followed by silver minerals, which generally do not maintain the colloform outlines belonging to the uraninite and inherited successively by chalcedony, sphalerite, and pyrite. Argentite generally follows pyrite in the sequence, and in places crystal terminations of pyrite protrude into the succeeding argentite. Chalcopyrite is closely associated with argentite, and was replaced by it to some extent. Argentite cuts across the earlier banded minerals of the filling and has replaced pyrite, sphalerite, uraninite (Fig. 22), and chalcedony as well as chalcopyrite; it also replaced included fragments of galena belonging to Stage A mineralization.

Proustite is closely associated with argentite and in a few cases was seen to have replaced it. Proustite, like argentite, cut across the earlier banded structure and replaced the earlier-formed minerals of Stage B, especially uraninite (Fig. 24). Native silver, found in the central portion of some vug fillings in fine wires, completed the silver mineral deposition but may represent near-surface oxidation. However, the lack of secondary uranium minerals and the position of the 1040 level well below the present water table render questionable a secondary oxidation origin for the wire silver and the earlier-described sooty uraninite.

In one polished section, small botryoids of uraninite surround euhedral crystals of proustite (Fig. 23) in a manner similar to the coating of sphalerite by uraninite described above. The appearance of this small amount of uraninite much later in the sequence than the bulk of uraninite deposition, like the previously described second generation of colloform uraninite deposited on sphalerite, is believed to be due to re-solution and redeposition of the earlier-formed material rather than a later hydrothermal introduction of uranium oxide, since the feature is quite local, and reworking of the relatively soluble uranium oxide by later vein solutions would be expected.

The complete sequence outlined above is not exhibited by all vein and cavity fillings studied. Certain minerals are omitted in the banded sequence of a given filling. In some cases pyrite lies directly against uraninite, with the normally present sphalerite missing (Figs. 7, 12); in others, uraninite and sphalerite are followed directly by proustite, with the omission of pyrite and argentite. A complete sequence may be observed in relatively few places.

Summary of Paragenesis.

From the evidence of open-space filling, cross-cutting relations and replacement features presented above, the order of deposition of minerals in the Radium Vein appears to be about as follows:

Stage A

1. Quartz with calcite and siderite
2. Pyrite?
3. Chalcopyrite
4. Sphalerite
5. Galena

Stage B

1. Gersdorffite and chalcedony
2. Uraninite and chalcedony (with minor pyrite)
3. Sphalerite and chalcopyrite (with minor pyrite and uraninite)
4. Pyrite
5. Argentite with chalcopyrite
6. Proustite (followed by very minor uraninite)
7. Native silver

Discussion of Ore Deposition in the Radium Vein.

Colloform Texture.—The more or less rounded outlines commonly shown by some minerals, variously termed spherulitic, botryoidal, reniform, or mammillary, have long been interpreted by many geologists as an indication of deposition by flocculation from a colloidal dispersion. The general term "colloform" was proposed in 1917 by Rogers (22) to describe textures characteristic of colloidal flocculates, referring only to the observable form and not whether the material was colloidal at the time of observation. The rounded outlines interpreted as colloidal are believed to be due to the action of surface tension on the flocculated material (2, p. 25). Lindgren (15) cited such rounded, colloform textures as an indication of deposition from the colloidal state, and even applied this term to similar textures apparently developed by colloidal replacement, which he termed "gel metasomatism." The widespread action of colloidal phenomena in the formation of the "kidney" iron ores, the colloform manganese oxides, some stalactitic forms of various carbonates, and colloform textures in many other mineral groups has been urged by Boydell (3), Rastall (20), Scott (27), and many others. In his recent book on interpretation of ore textures, Bastin (2, p. 20–32) includes a discussion of colloform textures and their significance. The interpretation of colloidal deposition has often been criticized because such textures are at best strongly suggestive, and the interpretation generally is not susceptible to proof.

"Pitchblende," the colloform variety of uraninite found in hydrothermal veins, almost invariably shows botryoidal or spherulitic textures. Colloform uraninite commonly shows further evidence of colloidal deposition in the presence of shrinkage or "syneresis" cracks. In their study of the mineralogy of the Great Bear Lake uraninite occurrence, Kidd and Haycock (13) accepted the botryoidal outlines and syneresis cracks as proof of deposition from the colloidal state. Evidence of radial and concentric shrinkage cracks is abundant in the botryoidal uraninite at Caribou.

Conformable banding of the succeeding sphalerite and pyrite on botryoidal surfaces of uraninite is also suggestive of colloidal deposition, as is the well developed colloform texture of chalcedony. In places, pyrite is finely inter-

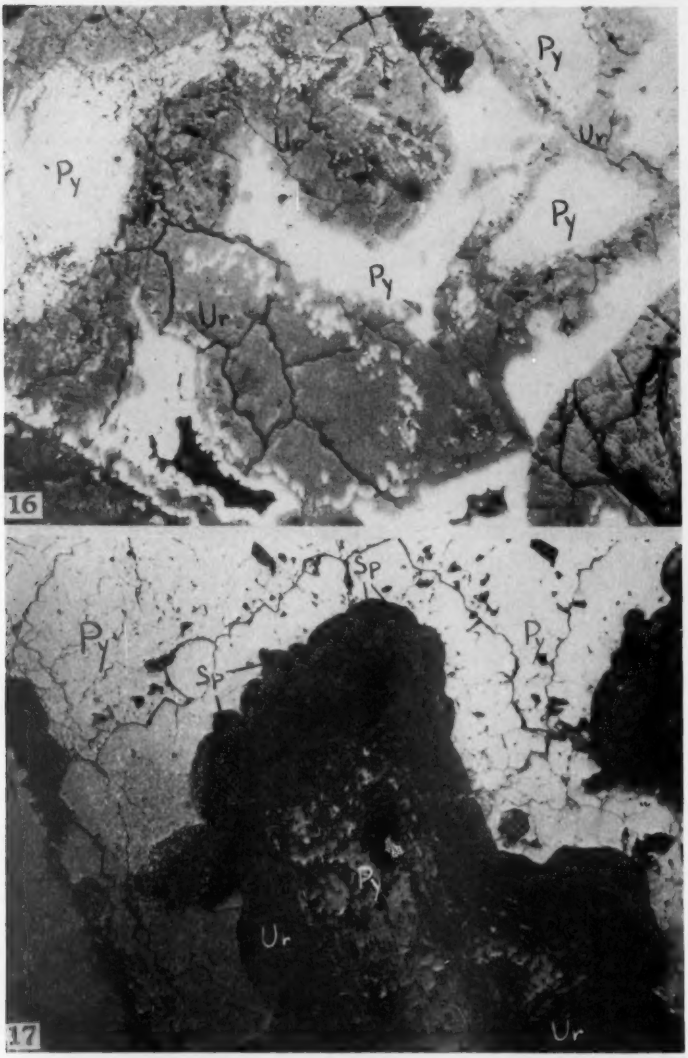


FIG. 16. Uraninite (Ur) veining and replacing pyrite (Py). × 100.
FIG. 17. Uraninite (Ur) coating and marginally replacing euhedral pyrite (Py) crystals of Stage A; uraninite replaced by sphalerite (Sp), followed by later pyrite. × 100.

banded with botryoidal chalcedony and uraninite. Bastin (2, p. 16), however, points out that some textures resembling colloform banding, as in the "Schalenblende" zinc ores of Aachen, Germany, owe their form to the underlying surface on which the minerals are deposited (crustification) rather than to rounding by surface tension.

The lack of shrinkage cracks in pyrite, sphalerite, and chalcedony in the Caribou ores throws doubt on an interpretation of colloidal origin for these minerals. Although the flocculates from lyophobic colloids (suspensoids) probably do not carry with them as much water as is present in the lyophyllic colloids (emulsoids), such as silica gel (2, p. 26), it seems probable that considerable water must be present in suspensoid flocculates if their surfaces are to be susceptible to rounding by surface tension. It seems probable that the escape of this water would result in shrinkage, which should be reflected in syneresis cracks. One further feature appears not to favor a colloidal mode of deposition of the pyrite and sphalerite: the pyrite and sphalerite bands are commonly several millimeters in width, which suggests successive deposits rather than simultaneous, thin, diffusion banding. The surface tension of flocculates of different materials might be expected to vary, which should result in different degrees of curvature at their surfaces. This should result in the formation of bands in which earlier botryoidal outlines would not be maintained by a succeeding flocculate having a different surface tension. From the foregoing evidence, the writer believes that the colloform-like texture of pyrite and sphalerite bands may be more easily explained by crystalline crustification on the earlier botryoidal uraninite surface than by colloidal deposition.

Textural evidence that uraninite in hydrothermal veins is normally deposited as a colloidal flocculate does not mean, of course, that uranium can be transported only in colloidal solution. Indirect evidence suggests that it may be carried in true solution as well, perhaps in the form of hydrated ion complexes. The extensive replacement of uraninite, especially by sphalerite, proustite, and argentite, suggests that uranium may readily be dissolved by hydrothermal solutions under some conditions. Uraninite is readily soluble in nitric and sulfuric acids. It seems doubtful that the penetration of altered wall rock by uranium, described previously, could have been accomplished by diffusion of colloidal size particles.

Temperature and Pressure Conditions of Formation.—Specific evidence closely delimiting the temperature-pressure conditions of formation was not found in the textures and mineral assemblage of the ores. The simple sulfide sequence—pyrite (?), chalcopyrite, sphalerite, galena—of Stage A mineralization contains no feature characteristic of a specific narrow temperature range, but suggests deposition under mesothermal conditions. The abundance of vugs and the open nature of the vein filling appear to indicate pressures no greater than those normally associated with deposition in the mesothermal zone. The chalcedony and silver minerals of Stage B mineralization suggest relatively low temperatures at the time of their formation, probably not higher than the low temperature portion of the mesothermal range.

Comparison with Other Hydrothermal Vein Uraninite Deposits.—The

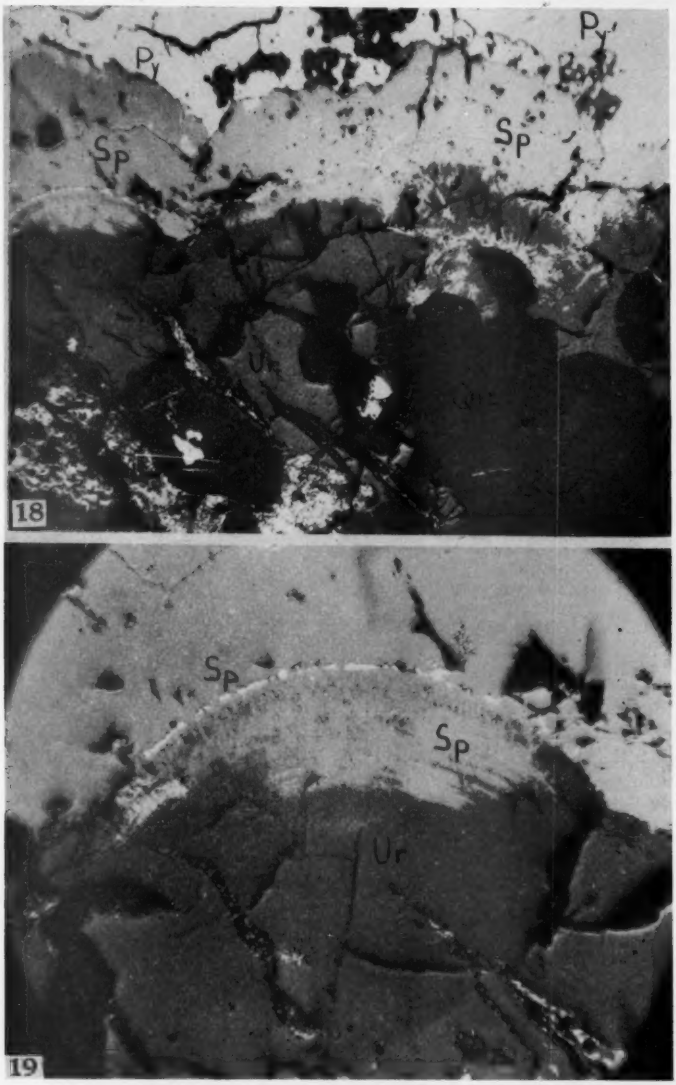


FIG. 18. Uraninite (Ur), sphalerite (Sp), and pyrite (Py) successively deposited on quartz (Qtz); uraninite partly replaced by sphalerite (note partly replaced uraninite botryoid near left margin). × 185.

FIG. 19. Higher magnification of sphalerite (Sp) replacing uraninite (Ur) botryoid in 8–1. × 550.

present study has sought information concerning the mineralogy of the Caribou uraninite occurrence chiefly along the lines of wall rock alteration, distribution of uranium in the wall rock, kinds and paragenetic relations of the vein minerals, and the character of the uraninite. Almost no studies of wall rock alteration and distribution of uranium in the wall rock adjacent to primary vein uranium deposits have been published, to the writer's knowledge. Detailed studies of the vein mineralogy and paragenetic relations have, however, been described from a fair number of localities. In all described vein uraninite occurrences, the uraninite is characterized by colloform texture, generally exhibiting both botryoidal outlines and syneresis cracks, which are commonly systematically arranged with respect to the botryoidal surface. The botryoidal material at some of these is accompanied by a fine, black, sooty or powdery form of uraninite.

Two features of uraninite deposits which may be compared on the basis of published mineralogical descriptions, and which show rather wide variation in different localities, are the nature and the paragenesis of the vein mineral assemblage. On the basis of the relatively small number of vein uraninite localities known prior to 1940, the Seventh Edition of Dana's System of Mineralogy (5) lists three characteristic "types" of occurrence (after Bastin) (1, p. 121–125):

(1) In high temperature hydrothermal tin veins. Uraninite occurs as colloform crusts associated with cassiterite, pyrite, chalcopyrite, arsenopyrite, galena, and cobalt-nickel-bismuth-arsenic minerals. This "type" is represented exclusively by Cornwall, England.

(2) In hydrothermal cobalt-nickel-bismuth-silver-arsenic veins formed at moderate temperatures. Uraninite is associated with pyrite, chalcopyrite, galena, carbonates, barite, fluorite, native bismuth, native silver and other silver minerals, smaltite-chloanthite, niccolite, and other compounds of cobalt, nickel, and arsenic. Notable occurrences are found at Joachimsthal, Bohemia; Johanngeorgenstadt, and Annaberg, Saxony, and Great Bear Lake, Canada.

(3) In hydrothermal sulfide veins formed at moderate temperatures, without cobalt-nickel minerals. Pitchblende is associated with pyrite, chalcopyrite, sphalerite, and galena. This type is known chiefly from Gilpin County, Colorado.

The number of "types" of vein uraninite mineral association based on known occurrences has been increased by discoveries within the past decade which do not conform closely to the types defined on the basis of the relatively few previously discovered occurrences, and will certainly continue to multiply as new mineral associations of uraninite are discovered. Thus, the deposit at the Sunshine Mine, Coeur d'Alene district, discovered in 1949 (30) shows uraninite associated with pyrite, arsenopyrite, argentiferous tetrahedrite, and chalcopyrite. This deposit has recently been studied in detail by Kerr (manuscript in press). At Marysvale, Utah (6, p. 71), where discovery of uraninite was made about the same time, a simple metallic mineralization of uraninite and pyrite was deposited with a gangue of quartz, fluorite, jarosite, and calcite. The associations at Coeur d'Alene and Marysvale, as well as those described in the present study at Caribou, Colorado and at Theano Point, Ontario, do not fit well with any of the three types listed above. With continuing studies of newly discovered deposits, it is found that uraninite may be associated with

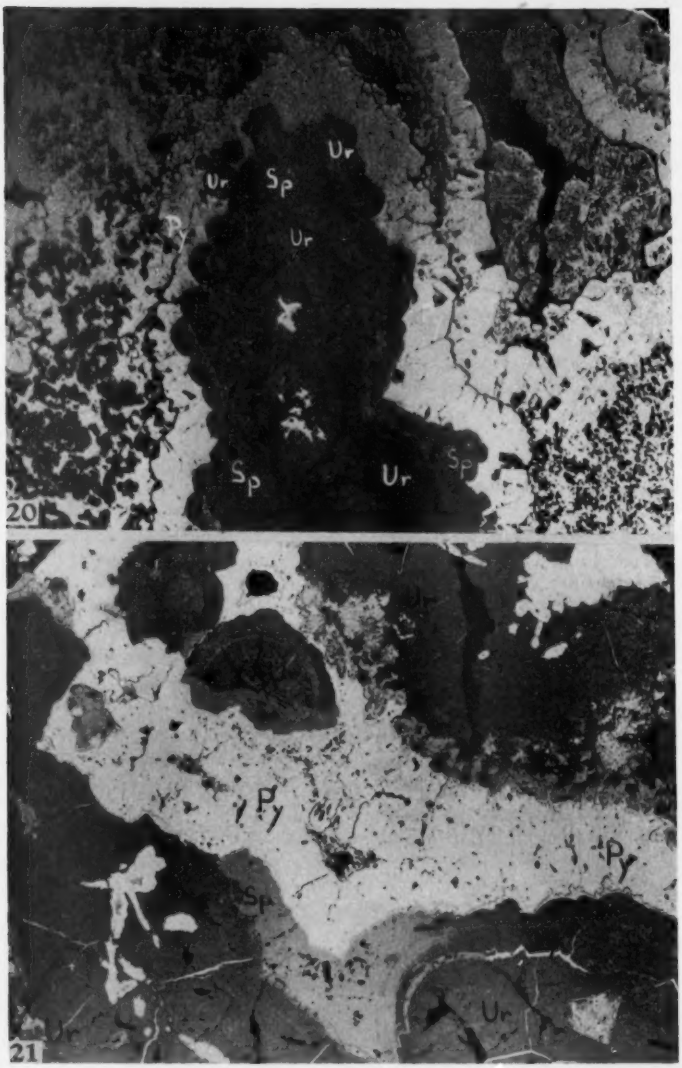


FIG. 20. Small uraninite (Ur) botryoids deposited on sphalerite (Sp) which extensively replaces uraninite of earlier, main period of deposition. These minerals are coated in turn by pyrite (Py) showing the typical conformable banding. × 100.

FIG. 21. Sphalerite (Sp) extensively replacing uraninite (Ur) along lines of botryoidal structure. Uraninite-sphalerite fragments engulfed by pyrite (Py) which also occupies fractures in uraninite. × 100.

a wide variety of minerals. However, on the basis of available information, it has been found (7) that minerals containing iron, copper, cobalt, lead, silver, nickel, and bismuth are the most common ore associates of vein uraninite. All but one of these—bismuth—are found in the Caribou deposit.

Since minerals of iron, copper and lead are extremely widespread in ore deposits, the less common cobalt, silver, nickel and bismuth are perhaps more useful "indicators" in prospecting for uranium. Cobalt-nickel minerals are represented in all but one district (Gilpin County, Colorado) representing the three "types" of association summarized above.

Although considerable similarity might be expected between the Tertiary uranium mineralization of neighboring Boulder (Caribou) and Gilpin (Central City) counties in Colorado, the differences are perhaps as striking. The sulfides pyrite, chalcopyrite, sphalerite, and galena are common to both. The presence at Caribou of a nickel sulfarsenide, gersdorffite, and the abundant silver minerals characterize the Caribou association as a more "typical" uranium ore suite than the neighboring Gilpin County deposit, in which silver and nickel are absent, as well as cobalt and bismuth.

In a recent comparison (6, p. 66–74) of twelve vein deposits of uraninite, based largely on published descriptions, uraninite was found to have a widely variable paragenetic position. At Great Bear Lake, uraninite is one of the earliest in a complex association of forty minerals, which includes all of the minerals found by the writer at Caribou. Early uraninite is found at Lake Athabaska, Canada, and at Shinkolobwe, Belgian Congo. By contrast, uraninite has been described as a late mineral at Coeur d'Alene, Idaho and Marysvale, Utah. In still others, such as the Front Range (including Caribou and Central City), uraninite is intermediate, having been deposited along with the sulfides. The writers attribute the variability of uraninite in the paragenetic sequence to its colloidal nature, with coagulation having been determined by chemistry of the individual ore solution rather than by falling temperature.

In summary, the association at Caribou of base metal sulfides, a nickel sulfarsenide, and silver minerals, is typical of many vein uranium deposits with regard to the metals present, and, of deposits described in the literature, most closely similar to Great Bear Lake in mineralogy. It differs from the Great Bear Lake association in having a much less complex mineralogy. A review of the paragenesis of uraninite ores reveals no characteristic sequential position of uraninite.

URANINITE AT CARIBOU.

Chemical Analysis.

Both the lustrous botryoidal and the dull-lustered, sooty uraninite described on preceding pages contain abundant fine-grained sulfides, as shown by polished section studies. Attempts at purification by froth flotation, magnetic separation, and microscopic hand-picking resulted in some concentration of the uraninite, but not a reasonably pure product. A partial chemical analysis [7]

[7] Obtained through Dr. C. J. Rodden, U. S. Atomic Energy Commission New Brunswick Laboratory.

gave the following results:

U_3O_8	40.77%
PbO	4.15
Fe_2O_3	3.15
CO_2	0.22
S	8.30

X-ray Analysis.

Debye powder patterns made on unconcentrated uraninite-rich samples gave strong lines for pyrite, but uraninite was obscured by the pyrite lines due to the somewhat similar face-centered cubic structure of the two minerals and their similar lattice constants. Recognizable uraninite lines were obtained only after concentration by flotation followed by microscopic hand-picking to remove pyrite. The powder pattern obtained agrees with uraninite, but the high angle lines are extremely diffuse, rendering difficult an accurate lattice constant measurement. Measurement of the three best patterns gave the lattice constants: 5.365 A°, 5.385 A°, and 5.398 A°. These fall at the lower end of the range of lattice constants of uraninite from various localities determined at Columbia University.

The variation in lattice constant is probably due at least in part to a variation in U^6/total U ratio in different samples of uraninite. In a recent study of six uraninite specimens from Lake Athabaska, Brooker and Nuffield (4) found a wide range in the ratio U^{6+}: total U, from 17.4 percent to 85.0 percent. As the U^6/U ratio increases, the specific gravity decreases, and the mineral shows progressive change from a hard, compact material to a soft, earthy form. The quality of the X-ray diffraction lines and the unit cell sizes also are related to the degree of oxidation of the uranium. The greater the U^6/U ratio, the more diffuse are the lines in X-ray diffraction powder photographs, and the smaller is the lattice constant. The lattice constant was found to vary progressively from 5.45 A° to 5.39 A° from lowest to highest U^6/U ratio, due to the smaller size of the U^{6+} than of the U^{4+} ion.

This work agrees with the results of studies of synthetic uranium oxides reported by Katz and Rabinowitch (11). In the face-centered cubic, fluorite-type lattice (corresponding to natural uraninite), a continuous isomorphous series from $UO_{1.75}$ to $UO_{2.3}$ was found. X-ray studies of artificial material ranging between the extremes of composition show increasingly diffuse x-ray diffraction lines and progressively smaller unit cell dimensions as the U:O ratio decreases.

The unusually diffuse x-ray diffraction lines and the small lattice constant described for Caribou uraninite agree well with the results of these studies, although specific determinations of U^4 and U^6 were not available for comparison.

SUMMARY AND CONCLUSIONS.

In the Caribou stock, in Boulder County, Colorado, the uraninite-bearing Radium Vein is surrounded by a halo of altered syenite. The sequence of

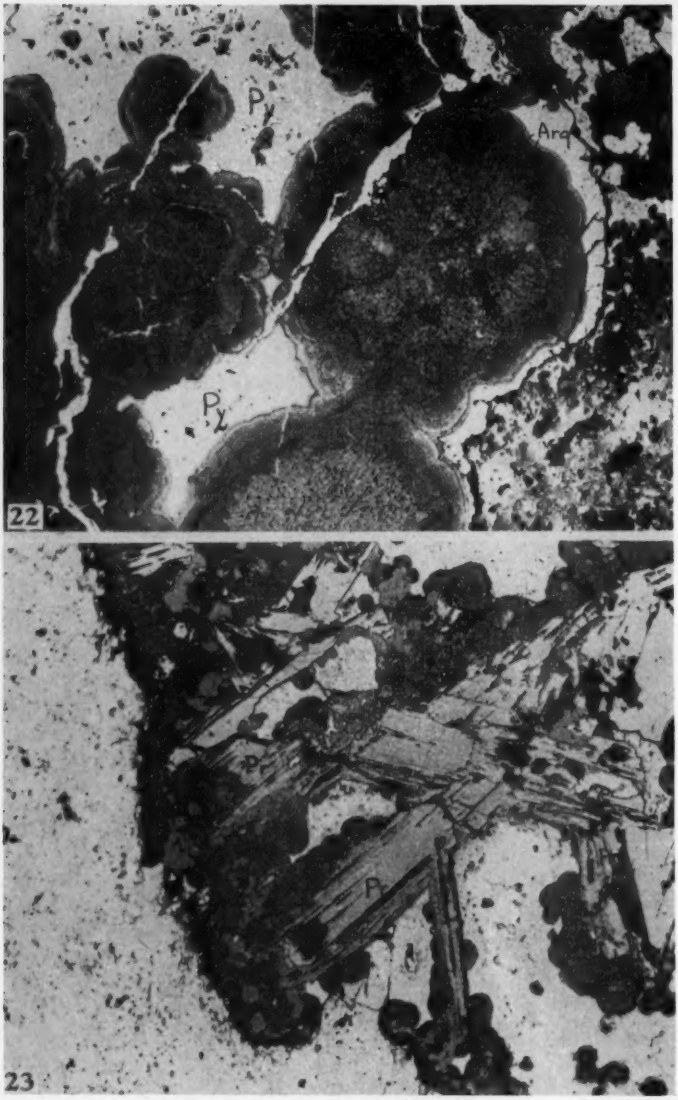


FIG. 22. Botryoidal uraninite (Ur) engulfed and cut by later pyrite (Py). Note displacement along pyrite veinlet, upper left. Argentite (Arg) replaces uraninite in central portion of botryoids. × 100.

FIG. 23. Small late uraninite (Ur) botryoids coating subhedral proustite (Pr) crystals. × 100.

alteration minerals, especially well developed on the hanging-wall side, is similar to that described at Butte, Montana by Sales and Meyer and at Boulder, Colorado by Lovering, with an early chloritic development (lacking in Lovering's sequence) followed successively by an argillic phase, a sericitic phase, and silicification adjacent to the vein. Certain broad features of alteration patterns associated with disseminated copper deposits in the Southwest, studied by Kerr and by Schwartz, were found to be similar to the Caribou pattern. The zonal arrangement at Caribou is complicated by the presence of a sericitic

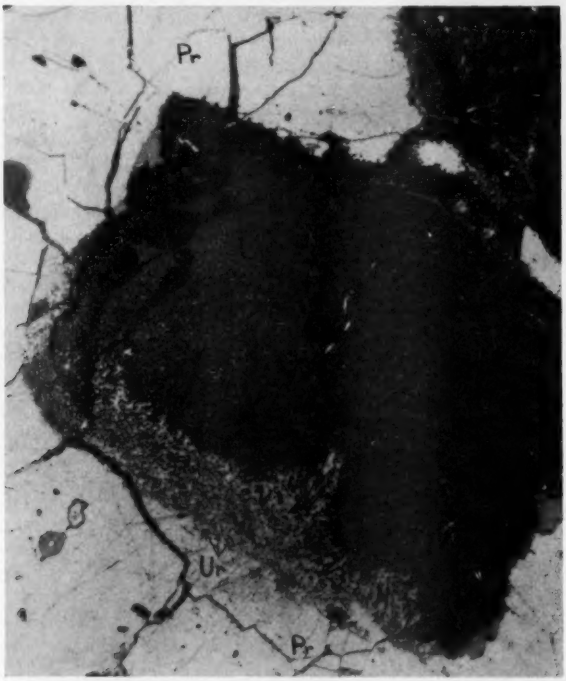


FIG. 24. Uraninite (Ur) replaced by proustite (Pr). × 250.

zone outside the argillized zone, as well as the more usual one between the argillized rock and the vein. It is thought that late vein solutions effecting sericitic development in the inner zone were prevented from permeating the argillized zone by the swelling of the abundant montmorillonite, but succeeded in crossing the argillized zone along fractures to penetrate and sericitize a band of rock beyond, forming a second sericitic zone.

The main chemical changes brought about in the wall rock by alteration were a progressive leaching of lime and soda, whereas potash, which was fixed

in the altered rock as sericite, shows largest values adjacent to the vein, where it was apparently augmented by vein solutions. Magnesia and alumina show little change across the altered rock, and silica generally increases in amount adjacent to the vein.

Alpha-counts together with chemical uranium determinations on wall rock samples indicate that uraninite deposition in the vein was accompanied by leakage into wall rock as far as the outer limit of alteration. Its distribution was controlled chiefly by the amount of porous rock available due to alteration, rather than by available fractures, and comparison with dissemination of lead and zinc suggests that the metals moved by ionic diffusion.

Hard, lustrous, botryoidal uraninite at Caribou was deposited early in the second of two stages of mineralization separated by a period of brecciation. During the first stage, chalcopyrite, sphalerite, galena, and possibly pyrite were deposited with a gangue of quartz, calcite, and siderite. The second stage began with gersdorffite, chalcedony, and uraninite, followed by sphalerite, chalcopyrite, pyrite, argentite, proustite, and native silver. A fine, porous, "sooty" uraninite fills later fractures and appears to represent reworking of the earlier-deposited material. The colloform texture of the uraninite apparently reflects its deposition as a flocculate from a colloidal dispersion, but sphalerite and pyrite bands showing similar form are intepreted as crustified layers that formed by crystallization rather than colloidal deposition. Textural evidence and mineral association suggest that the ores belong to the lower temperature portion of the mesothermal range.

Lattice constants measured from three x-ray powder patterns of Caribou uraninite—5.368 A°, 5.385 A°, and 5.398 A°—fall at the lower end of the range for uraninite reported from a number of localities. The relatively small unit cell dimensions and the diffuse x-ray diffraction lines are in harmony with studies reported by Brooker and Nuffield and by Katz and Rabinowitch.

ACKNOWLEDGMENTS.

This study was made under the supervision of Professor Paul F. Kerr of Columbia University, director of the project. His continued advice and suggestions are gratefully acknowledged. Professor Charles H. Behre of Columbia University made available the facilities of the polished section laboratory and provided helpful information on techniques for polished section studies. Professor J. Lawrence Kulp made available alpha-scintillation counting equipment at the Lamont Geological Observatory. Dr. Donald L. Everhart, of the U. S. Atomic Energy Commission, furnished much help in the formulation of plans for the study, and aided greatly in the field reconnaissance and collection of samples. The writer is indebted to Professor John D. Ridge and Thomas F. Bates of Pennsylvania State College for helpful discussion of ideas and interpretations.

Mr. Robert King of the U. S. Geological Survey and Mr. Charles Towle of the U. S. Atomic Energy Commission furnished information based on their field studies, and helped to obtain suitable samples. Mr. Elmer Hetzer, Mine Superintendent at Caribou, donated a number of specimens of high-grade

uraninite ore, and several fine specimens were loaned by the AEC Raw Materials Operations Office in New York. The work was partially done under Columbia University Contract No. AT (30–4) 702 with the Division of Raw Materials, U. S. Atomic Energy Commission.

PENNSYLVANIA STATE COLLEGE,
DEPARTMENT OF EARTH SCIENCES,
STATE COLLEGE, PA.,
August 9, 1953.

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TRANSPORTATION AND DEPOSITION OF QUICKSILVER ORES IN THE TERLINGUA DISTRICT, TEXAS.[1]

GEORGE A. THOMPSON.

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ABSTRACT.

The geologic relations of the Terlingua quicksilver deposits, considered together with more general chemical and physical limitations, serve to indicate the probable mode of transportation and causes of deposition of the ore. In the zone of deposition, the ore-bearing fluid was a liquid or a mixed liquid and vapor, as shown by replacement of limestone. Deposition at a representative depth of 900 feet took place under the following probable conditions: a fluid pressure of about 30 atmospheres (certainly less than 66 atmospheres); a temperature near 200° C (certainly less than 286° C). The ore-bearing fluid contained sulfur, chlorine, iron, ammonia, and at least 10^{-5} percent of mercury (0.1 part per million). It had a pH greater than 6. Concentration of a large part of the ore beneath relatively impermeable rocks was caused by hydrodynamic conditions that involved floating of the ore-bearing fluid on cooler and heavier meteoric water, thus largely restricting the ore-bearing fluid to the upper part of the permeable zone. Precipitation of cinnabar may have been caused by changes in temperature and pressure in the presence of a gas phase, by dilution, and to a small extent by chemical reaction with clay. Supersaturated or colloidal solutions are postulated to explain the sporadic distribution of ore on a small

[1] Publication authorized by the Director, U. S. Geological Survey.

scale, and a catalytic effect of the clay on supersaturated solutions is suggested.

INTRODUCTION.

Krauskopf (1)[2] has studied the physical chemistry of the possible vein fluids that could deposit quicksilver ores. Considering all possible fluids capable of transporting mercury at temperatures higher than 250° C and pressures greater than 30 atmospheres, and capable of depositing the mercury in response to physical and chemical changes, he concludes that the possible mechanisms are: transportation as a complex ion in slightly alkaline sulfide solutions, as the volatile chloride, and as mercury vapor. Two other mechanisms, supersaturation and colloidal dispersion, cannot be evaluated by ordinary methods of chemical thermodynamics. The present paper is an attempt to correlate and test Krauskopf's findings with the geologic occurrence of quicksilver ores in the Terlingua district, in the Big Bend area of western Texas.

The Terlingua district, formerly one of the principal quicksilver-producing districts of the United States, is an area of limestones and shales of Cretaceous age, which have been invaded by a variety of hypabyssal intrusions. The predominant ore mineral, cinnabar, is associated with steeply dipping faults and fissures and with masses of breccia attributable to solution of limestone. A large part of the ore has come from intersections of steep fractures with the flat or gently dipping contact of the thick Devils River limestone with the overlying calcareous clay shale. Both the shale and the limestone served as host rocks.

The geology of the Terlingua district and its ore deposits is described by C. P. Ross (2) and by Yates and Thompson (3).

PHYSICAL AND CHEMICAL CONDITIONS OF DEPOSITION.

The physical and chemical conditions under which the ores were transported and deposited are in part indicated by the geologic relations. To be sure, the evidence is unsatisfactory or incomplete in many instances, but combined with evidence on other ore deposits and with general physico-chemical restrictions, the geologic evidence leads to useful general conclusions. Important conditions to be considered are: the phases present (whether vapor, liquid, or both), the pressure, the temperature, the hydrogen-ion concentration, the composition of the transporting fluids, and their concentration.

Phases.—A considerable part of the cinnabar in the Terlingua deposits is a replacement of limestone and calcareous shale; calcium carbonate was removed as cinnabar was deposited. Vapor transport of calcium carbonate seems extremely improbable at the low temperatures of quicksilver deposition, therefore deposition of the ores from a liquid or from a mixed liquid and vapor is indicated.

Weight for weight, the mercury-transporting capacity of an alkaline sulfide solution (pH 9 and total dissolved S 0.1 mole/liter) and of water vapor at

[2] Numbers in parentheses refer to References at end of paper.

127° C is about the same (1). This means that in a two-phase hydrothermal fluid composed of liquid of this pH and sulfur content, and gas (water vapor) at this temperature, most of the mercury would be in the liquid unless the weight of gas exceeded the weight of liquid, under which condition the volume of gas would, of course, be much greater than the volume of liquid. At a temperature of 200° C, equal volumes of gas and liquid would carry approximately equal amounts of mercury. There is no direct evidence to determine whether or not the proportion of gas was actually this high, nor does the temperature-pressure data discussed in later sections answer the question, but on general grounds it is reasonable to believe that the liquid phase predominated in the zone of deposition. The ore-bearing fluid came into permeable rocks at depths where cool meteoric water would normally be present; admixture of meteoric water with the ore-bearing fluid is probable and would increase the proportion of liquid. Comparison with hot springs, most of which discharge a greater volume of liquid than gas, leads to the same conclusion. The replacement ore in the Terlingua deposits indicates that deposition was at least partly from a liquid; general relations suggest that the liquid phase was predominant.

Pressure.—The maximum vertical range of the deposits in any one mine in the Terlingua district is from the surface to a depth of a little less than 900 feet, but the amount of post-ore erosion is not known. The known depth range of quicksilver deposits the world over is from the surface to 1,950 feet, the deepest being New Almaden in California, where the lowest deposits are approximately 1,950 feet below the highest, according to E. H. Bailey (oral communication). The majority of quicksilver deposits are relatively shallow; the Almaden mine, in Spain, reached 1,300 feet in 1948; Idria is less than 1,000 feet deep; and New Idia is 1,400 feet deep. The most reasonable explanation of the present shallow depth range is that the depth range at the time of deposition was also characteristically shallow. This suggests that post-ore erosion at Terlingua amounted to only a few hundred feet. A depth of 900 feet in all probability represents the depth of cover of some part of the deposits at the time of deposition. The pressure limits for this depth can be treated as a specific case, recognizing that one cannot identify the part of the deposit for which the limits are being established until the amount of post-ore erosion is known. If post-ore erosion amounts to as much as 900 feet, the pressure limits established will apply to deposits at the present surface; if post-ore erosion is less, the limits apply to deposits somewhere between the present surface and 900 feet. The exact depth makes little difference because the deposits show no systematic changes with depth.

The pressure at the 900-foot depth was probably at least equal to the hydrostatic head of 900 feet of water, somewhat less than 27 atmospheres if the water was hot. This figure should be reduced if the fluid was partly vapor, but, as previously noted, a large proportion of the fluid was probably liquid. The maximum pressure, on the other hand, could not have been appreciably greater than the pressure due to the weight of the overlying rocks, the lithostatic head, because the tensile strength of sedimentary rocks, particularly across the bed-

ding planes, is low. For 900 feet of rocks of density 2.5, the maximum pressure would be 66 atmospheres.

In addition to absolute pressure, the pressure variation from place to place might be important. Under conditions of dynamic flow, the pressure varies depending on the velocity of the liquid. By the law of conservation of energy, at any point in a tube through which a liquid is flowing, the sum of the pressure energy, the gravitational potential energy, and the kinetic energy, per unit volume, is a constant (neglecting friction). This is expressed by the familiar theorem of Bernoulli:

$$p + hdg + 1/2\, dv^2 = \text{ a constant,}$$

where p is pressure; h, height above a reference plane; d, density of the liquid; g, the force of gravity; and v, velocity of flow. The change in pressure resulting from a change in velocity can be evaluated from the third term of the equation. If the velocity of liquid of density 1.0 were increased from zero to the improbably high velocity of 1,000 centimeters per second, the pressure would be decreased by 5×10^5 dynes per square centimeter, or only 0.5 atmosphere. This factor is apparently too small to be important.

The change in pressure due to the work done against gravity is given by the second term of the equation. From this it can readily be seen that the pressure change when the liquid rises is just equal to the change in hydrostatic pressure. Any additional pressure loss must therefore be due to frictional loss, which is neglected in the equation. If it is assumed that the pressure at any given depth did approach the lithostatic head, a major part of the pressure drop between that depth and the surface would have to be accounted for by frictional loss of energy. At a constriction in the channel, the pressure might decrease from a value approaching the lithostatic head below the constriction to a value approaching the hydrostatic head above the constriction. Under such extreme conditions, actual erosion of the channel and mechanical upward transport of particles of rock might logically be expected in some places, but no evidence of this has been observed in any of the mines. Another consideration arises where the channels vary from large openings extending through a vertical range of hundreds of feet in limestone, to constricted channels in overlying shale. Throughout the large channels the pressure gradient due to friction must have been relatively small, and inasmuch as the pressure could nowhere exceed the lithostatic head it follows that the pressure in the deepest part of the large channels must have been considerably less than the lithostatic head at that depth.

The pressure was therefore probably not much less than 27 atmospheres and certainly not greater than 66 atmospheres at the representative depth of 900 feet. The pressure may have decreased gradually or in sudden steps toward the surface, and the minimum pressure may have approached surface conditions.

Temperature.—The best evidence on the minimum temperature of deposition of the Terlingua ores is provided by the inversion temperatures of the mercury ammonium chlorides kleinite and mosesite. Evidence on the maximum temperature of deposition is provided by the temperatures of decompo-

sition of these minerals and of the mercury oxide montroydite, and upper temperature limits are set also by the melting temperature of the mercury chloride calomel and by the boiling point of water under the existing pressure.

Kleinite and mosesite, common only at the Mariposa mine, are rarely in actual contact with the principal ore mineral, cinnabar. Cinnabar generally occurs only a few inches or a few feet away in the same fracture system, however, and the geologic relations are such as to leave little doubt that the time and physical environment of deposition were similar, although not necessarily identical. Mercury chlorides are probably more widespread and abundant than has been recognized, for chemical tests of cinnabar ore from several mines showed the presence of chloride (2, p. 140).

According to Hillebrand and Schaller (4), kleinite is geometrically hexagonal, but the internal structure does not agree with this form for a basal section shows double refraction. During slow heating of a basal section of the mineral the double refraction disappears at a temperature of about 130° C, but upon cooling and standing for several months the mineral returns to its doubly refracting condition. This phenomenon shows that the hexagonal crystals of kleinite must have been formed at a temperature above 130° C. Kleinite decomposes in the laboratory between 260° and 280° C.

Mosesite, another mercury ammonium chloride, has the crystal form of an isometric mineral, but the internal structure, like that of kleinite, does not agree with the external form, because mosesite is doubly refracting (5). The double refraction disappears when mosesite is heated to 186° C, indicating that the mineral was deposited at a temperature above 186° C.

In these shallow deposits it is probably safe to neglect the effect of pressure on the crystallographic inversion temperatures and to conclude that kleinite and mosesite were deposited at minimum temperatures of 130° and 186° C, respectively. The decomposition temperatures of the mercury minerals, in contrast to the inversion temperatures, may be strongly influenced by other physical and chemical conditions and may not be a reliable index of maximum temperature. A more dependable indicator of the upper temperature limit is the melting temperature of calomel, 302° C. Although it is conceivable that mercuric chloride could be deposited as a liquid at high temperature and crystallized later, good-sized calomel crystals on the walls of open vugs could not have been originally deposited as a liquid in that location.

It is interesting to note that the minimum temperatures necessary to form kleinite and mosesite, 130° and 186° C respectively, could have been attained in the presence of liquid water only if the pressures were at least 1.7 atmospheres and 11.3 atmospheres respectively, equivalent to hydrostatic heads of 54 feet and 385 feet of cold water, or somewhat greater heads of hot water. The fact that these minerals are now found at and near the surface indicates that several hundred feet of rocks have been eroded from the Mariposa mine area since deposition of the mosesite, providing the assumption of liquid water being present is correct. (Unlike cinnabar, kleinite and mosesite were not observed as a replacement of limestone and this evidence of deposition from a liquid phase is lacking.) The depositional environment of cinnabar, in con-

trast to that of mosesite and kleinite, may have extended to shallower depths and lower temperatures.

At the representative depth of 900 feet for which the pressure data have been discussed, there is a maximum temperature at which a liquid phase could exist. At a pressure of 27 atmospheres, liquid water would not exist above 231° C; and at the extreme pressure of 66 atmospheres, liquid water would not exist above 284° C. These temperatures would probably be modified only a few degrees by the presence of salts in solution, for the molal boiling point constant of water is only 0.52° C.

The temperature limits 130° to 284° C are not to be considered as bracketing the possible deposition temperatures of cinnabar. They are, however, a clue to the temperature of deposition of the Terlingua ores, and as such they are in substantial agreement with independent estimates for other areas. Dreyer (6), for example, suggests 100 to 150° C as the usual temperature limits, but his discussion emphasizes deposits with a depth range of only 0 to 200 feet.

Hydrogen-ion Concentration.—Evidence on the hydrogen-ion concentration of the ore-forming fluid may be inferred from the composition of the wall rocks and the vein minerals. Below the main zone of ore deposition in the Terlingua district is limestone more than 1,000 feet thick, through which the ore-bearing fluid must have risen. Fluids that traveled this far in limestone, through channels that are not coated by noncarbonate minerals, could not have remained strongly acidic. Reaction with the limestone would neutralize any strong acid originally present, and the equilibrium pH would depend largely on the partial pressure of CO_2. It will be convenient to compare the hydrothermal solution with sea water. The pH of sea water in equilibrium with the atmosphere and saturated with calcium carbonate is close to 8.0 (7, 8, 9). If the partial pressure of CO_2 is raised by a factor of over 3000, from the pressure of CO_2 in the atmosphere (3×10^{-4} atmosphere) to 1.0 atmosphere, the pH is decreased to 6. A limiting case for the purposes of this paper would be cool water in equilibrium with pure CO_2 at 27 atmospheres. Extrapolating Rubey's curve (9) gives a pH between 5 and 6, and this value is obviously too low because the ore-bearing solution was hot and probably contained other gases. It may be concluded therefore that the pH of the ore-bearing solution was 6 or greater.

Next, were the solutions strongly alkaline? Distilled water free of carbon dioxide reacts with calcite to give a solution with a pH of 9.0 (10); the pH would be lower if carbon dioxide were present, as discussed above. If the fluids entering the limestone were neutral or acidic, reaction with limestone could result in a pH no higher than 9.0; and because of the probable presence of CO_2, either originally in the fluids or produced by reaction of acidic fluids with limestone, the resultant pH would probably be considerably less than 9.0. On the other hand, if the fluids entering the limestone were already strongly alkaline, they would tend to remain so; this was confirmed experimentally by adding calcium carbonate to various solutions having pH greater than 12—no change in pH occurred.

The thick section of limestone in the Terlingua district is succeeded by clay

shale, and a strongly alkaline solution traversing shale would tend to have its pH reduced by exchange of the metal ions in the solution for hydrogen ions in the clay. The final pH of strongly alkaline solutions after reacting to equilibrium with a large volume of clay would approach the pH of the same clay in a small amount of distilled water. Bassett (11) determined the pH of several clays by suspending 200 milligram samples in 35 cc of distilled water. She found a pH range of 5.8 to 6.6 for four kaolinite samples, 6.5 for one illite, and 7.5 to 8.2 for four montmorillonite samples. The writer used the same technique on clays from the Terlingua district and obtained pH readings of 6.5 to 7.0. These clays would be expected to react with strongly alkaline solutions to reduce the pH. Because of the low permeability and quite limited reactive capacity of the clays, however, it is not safe to infer any definite pH limits for a solution that has passed through clay.

The evidence in the Terlingua district thus suggests an ore-bearing fluid of pH greater than 6 but gives no indication of the upper limits of possible pH. A near-neutral fluid would be compatible with general evidence that fluid inclusions in minerals are not strongly alkaline.

Composition.—The composition of the ores and wall rocks provides scant direct evidence of the composition of the ore-bearing fluids, for little or no trace is left of the most soluble constituents. Sulfur, mercury, iron, chlorine, and, locally at least, ammonia were present, for all these substances are present in the minerals of the deposits. Chlorine was a more widespread constituent than is easily recognized from the mineralogy, for mercury chloride was found by chemical analysis in samples of cinnabar ore from various mines (2). The abundance of chloride in hot springs the world over is well known (12, 13), and many hot springs are primarily sodium chloride waters with widely varying amounts of other constituents. A predominance of sodium chloride is also often reported in fluid inclusions in minerals (14). Taking all the evidence into consideration, it is reasonable to infer that the ore-bearing fluids in the Terlingua district were hydrous, neutral or alkaline, chloride- and sulfide-bearing fluids containing also several metal ions.

Concentration of Mercury.—Krauskopf (1) has taken a concentration of 10^{-7} grams of mercury per liter of solution, or about 10^{-8} percent as an extreme minimum below which a solution could not be effective in transporting quicksilver ores. The importance of this assumed minimum concentration is that it fixes the demands that must be made upon any mechanism of transportation. If, for example, the actual concentration were far greater than the assumed minimum, certain mechanisms that have been considered possible might be eliminated. For this reason it seems worthwhile to reexamine the problem of minimum concentration, although the evidence in the deposits themselves is extremely scanty.

One general approach to the problem may be made through a consideration of the amounts of mercury and of water given off during the crystallization of a magma. Ideally, a comparison of analyses of glassy and crystalline phases of the source rock should give an indication of the amount of mercury given off during crystallization, but at present no such paired analyses of any rocks are available. The mercury content of igneous rocks as reported by Saukov

(15), Preuss (16), and Stock and Cucuel (17) is 10^{-6} percent to 10^{-5} percent, the difference between these two figures being also about 10^{-5} percent. It might be assumed that a crystallizing magma gave off 10^{-5} percent of mercury along with 3 percent of water, this amount of water being an intermediate value among estimates by several investigators (9, p. 1137). The concentration of mercury in the magmatic water is then $\frac{10^{-5}\%}{3\%} \times 100 = 3 \times 10^{-4}\%$. Following Rubey's calculation of heat loss by dilution (9, p. 1139), the magmatic water may have been diluted by as much as 8 or 9 parts of meteoric water before reaching the temperature of deposition. On these assumptions the mixture would contain 3×10^{-5} percent of mercury.

A second general approach to the problem of concentration is suggested by the high mercury content of shales. Average shale contains 5×10^{-5} percent mercury according to Stock and Cucuel (17) and 3×10^{-5} percent according to Preuss (16); this is five to ten times as much as in average igneous rocks. In the conversion of an average shale to a high-grade metamorphic rock or to a plutonic rock, presumably about 3×10^{-5} percent of mercury would be driven off (the difference between the content in shales and in plutonic rocks), along with about 3 to 4 percent of water (difference between amount in shales and in plutonic rocks). The concentration of mercury in the water would be 10^{-3} percent, or, if diluted by 9 parts of meteoric water, 10^{-4} percent. This figure (and the closely comparable one derived above from the crystallization of a magma) is obtained by utilizing averages applicable to ordinary rocks, whereas quicksilver deposits are relatively rare. From this standpoint the calculated concentrations might be considered minimum figures.

A crude test of the calculated minimum can be made on another basis. The smallest openings that have been filled with cinnabar are microscopic in dimensions and it is not unusual to find cinnabar deposited in a thickness of a millimeter or less in tight fractures that can be followed for tens of feet. As Hubbert (18, p. 802) has pointed out, friction damps out any large velocities of ground-water motion in such small channels. The flow velocity is commonly of the order of a few centimeters per day, let us say not more than 1,000 cm per day for the smaller channels under consideration, even though the viscosity may be lower and the head higher for hydrothermal solutions. Let us assume that the solution, containing 3×10^{-5} per cent of mercury, deposits all its mercury as cinnabar in 100 cm of flow, or 1/100 of the total in each centimeter. The fraction of the volume that is filled each day is

$$\frac{1/100 \times 1000}{\text{density of HgS} \times \%\ \text{Hg in HgS}} \times 3 \times 10^{-7} = \text{approximately } 4 \times 10^{-7},$$

and the channel will be completely filled in 2×10^{6} days or 5×10^{3} years. Geologic evidence indicates that the deposition of cinnabar took place in a short time compared to other events such as the formation of calcite veins. We infer, therefore, that the concentration of 3×10^{-5} percent of mercury is indeed a minimum concentration—it is difficult to conceive of a more dilute solution producing the observed geologic results in a reasonable geologic time.

The amount of solution of this concentration required to produce a quicksilver deposit or group of deposits containing 50,000 76-pound flasks of mercury is $\frac{50{,}000 \times 76}{3 \times 10^{-7}}$ or 1.2×10^{13} pounds. This is equivalent to $\frac{1.2 \times 10^{13}}{62.4}$ or 2×10^{11} cu ft of water, containing 2×10^{10} cu ft of magmatic water. The required volume of magma of density 156 pounds/cu ft and evolving 3 percent of water is

$$\frac{\frac{100}{3} \times .1 \times 1.2 \times 10^{13}}{156} = 2.5 \times 10^{11} \text{ cu ft, or approximately 2 cubic miles.}$$

Despite the shaky assumptions in the foregoing paragraphs, the several independent lines of evidence are in harmony. The time and the volume of magma required are not unreasonable and thus they support the conclusion, based on the mercury content of rocks, that the ore-bearing fluids carry at least 10^{-5} percent of mercury. Expressed in another way the ore-bearing fluids contained at least 0.1 part per million of mercury by weight. By way of comparison, ordinary rain water contains 0.002 part per million of mercury (17), and even this small amount is 20 times the concentration adopted by Krauskopf as a safe minimum.

Krauskopf's data show that an alkaline sulfide solution is capable of dissolving 0.1 part per million of mercury (5×10^{-7} mole/liter) if it has a pH of 9 and total dissolved sulfide of 0.1 mole/liter, or a higher pH with lower sulfur content (1, p. 503). Compared with the pH and sulfur content of thermal springs and fluid inclusions in minerals, the required pH and sulfur content seem to be excessively high, but the data are not sufficiently complete or accurate to be conclusive.

On the other hand, calculations based on Krauskopf's data indicate that water vapor at 227° C is capable of carrying considerably more than 0.1 part per million (by weight) of mercury. This is true even at a pressure of 26 atmospheres, which would be required for the water vapor to be in equilibrium with liquid water.

THE ROLE OF VARIATIONS IN ROCK PERMEABILITY.

Variations in rock permeability have been pointed out by many writers as a factor in the localization of ore deposits. Relatively impermeable rocks in particular have been described as "impermeable barriers" or diversion dams beneath which ores have been concentrated. Many of the quicksilver deposits in the Terlingua district are found near the top of permeable limestone or near the base of the overlying, relatively impermeable shale. On the basis of his work in this district, Udden (19) long ago proposed an anticlinal theory of ore accumulation closely analogous to the anticlinal theory of petroleum accumulation. In spite of the long history of interest in permeability variations no completely satisfactory theory has so far been proposed to account for their role in ore deposition.

In rocks of contrasting permeability, moving water tends to be confined to the permeable rocks—the aquifers. This is true in any case, whether the permeability is original as in a sandstone, or secondary as in a cavernous limestone or a fractured rock. Mining geologists are accustomed to the concept of permeable fracture zones, and the detection and projection of such zones constitute one of the principal methods of search for new ore deposits. At Terlingua, the limestone contains permeable fracture zones enlarged by solution, but the fractures in shale are tight and relatively impermeable. These conditions, however, do not in themselves explain the common occurrence of epithermal ore deposits at the top of an aquifer, directly beneath an impermeable stratum.

It has generally been assumed that vein fluids tend to rise in an aquifer and collect or migrate along the top of the aquifer, directly beneath an impermeable barrier. This pattern of flow is seemingly required by the distribution of ore deposits, but it is not the pattern of flow to be expected of a homogeneous fluid in a uniform aquifer. The flow of ore-bearing fluids could be concentrated at the top of an aquifer for one of two reasons: either the permeability is greater at the top of the aquifer, or the aquifer contains two or more fluids of differing density, with a lighter fluid floating on a heavier fluid.

In the Terlingua district the top of the main aquifer, the Devils River limestone, is not sufficiently more permeable, in the writer's opinion, to explain the localization of ore at the top. Large pre-ore fissures can be followed downward from the top of the limestone for hundreds of feet, but they rarely contain ore deposits except near their tops. These relations could be explained by deposition of the ore from a gas floating on a liquid, as Newhouse (20, p. 53) has pointed out. They could equally well be explained by hot water floating on cooler water of greater density. Reasons have already been stated for believing that the Terlingua ores were deposited at least in part from a liquid. Moreover, any general explanation for ore deposits beneath impermeable barriers will have to be valid for ores of several metals, not just quicksilver deposits. For ores of some of these metals, deposition from a gas phase is extremely unlikely. The general explanation of ores directly beneath impermeable barriers seems therefore to be either in permeability differences within the aquifer—which are probably not adequate—or in density differences between two liquids.

Ore-bearing hydrothermal solutions in the epithermal zone invade volumes of rock that are normally occupied by cool meteoric water. The normal hydrodynamic conditions are modified by the rising hot water, and the resultant flow pattern is a combination of both influences. The inference of hot water floating on cooler water is actually what would be expected. Hot ore-bearing fluids entering an aquifer filled with meteoric water and overlain by an impermeable stratum would tend to rise in columns through the cooler meteoric water and spread out at the top of the aquifer, for the reverse situation is mechanically unstable. White and Brannock (21, p. 573) describe the convection system at Steamboat Springs, Nevada, in the following way. "The same fault or fault zone may be utilized by both the up-flowing saline

water and the down-flowing meteoric water, and is comparable in many ways to a huge convection system; the central part of the system is extremely hot, so the average density of the water is relatively low in spite of its salinity; laterally from the central core but still within the fault system and adjacent strata, meteoric water is migrating inward and downward. Its average density is perhaps five to ten percent greater than that of the saline water because of its low temperature."

Hubbert (18) has elucidated the general tools for working with such a system. His theoretical treatment applies to any fluids, and his calculations on a system composed of sea water, fresh water, and air are applicable to a system composed of cool water, hot water, and gas. We are interested in the form assumed by the body of hot water—the ore carrier—and particularly in the slope of the interface between hot water and cold water. Considering the potentials and components of flow parallel to the interface in a vertical plane section through the system (Fig. 1), and calling α the angle of slope measured positively upward, gives (18, p. 865): [3]

$$\sin \alpha = \frac{1}{g}\left(- \frac{\rho_2}{\rho_2 - \rho_1} \cdot \frac{q_{2s}}{\sigma_2} + \frac{\rho_1}{\rho_2 - \rho_1} \cdot \frac{q_{1s}}{\sigma_1} \right)$$

where g is gravity

ρ_1 and ρ_2 are the densities of the less dense and more dense fluids, respectively.

q_{1s} and q_{2s} are the components in the direction s of the rates of flow per unit area of the less dense fluid and more dense fluid, respectively, in the section we are considering.

σ_1 and σ_2 are the conductivities of the less dense and more dense fluids, respectively. (The conductivity is equal to $k \cdot \frac{\rho}{n}$ where k is the coefficient of permeability, ρ is the density of the fluid and n is its viscosity.)

Meteoric water moves generally from higher to lower elevation within the confines of an aquifer, for the driving force is gravity. On the other hand, hot water entering a permeable rock already occupied by heavier meteoric water tends to move, with some intermixture, from lower to higher elevation until it floats on the meteoric water. The equation shows that under these conditions —when the two fluids flow in opposite directions—the component tilts due to the flow of each fluid augment one another and the resultant is greater than that due to either alone. The main factors tending to cause large tilt of the interface between two liquids are low conductivities (favored by low permeabilities) and large rates of flow.

The relations that have been outlined provide an adequate explanation for the occurrence of ore at the top of a permeable body of rock, beneath an "impermeable barrier," a most important type of deposit in the Terlingua district.

[3] The formula given by Hubbert is corrected to include separate σ_1 and σ_2 for the individual fluids.

Sufficient data are not available to test the details of the theory on a particular deposit, but it may be worthwhile to point out how this might be done.

Some epithermal deposits may have undergone so little erosion that significant older hydrodynamic conditions can be inferred from present conditions. From observations of normal ground-water levels, the present hydraulic gradient can be plotted. If it can be assumed that the present movement of ground water is similar to that before hydrothermal activity, or if the differences can be roughly estimated, the present hydraulic gradient or slope of the water table becomes a guide to conditions during ore deposition. Because the flow of hot water is likely to be opposite to that of the cold meteoric water, the slope of the interface between the two liquids will generally be greater than the measured hydraulic gradient. A rough indication

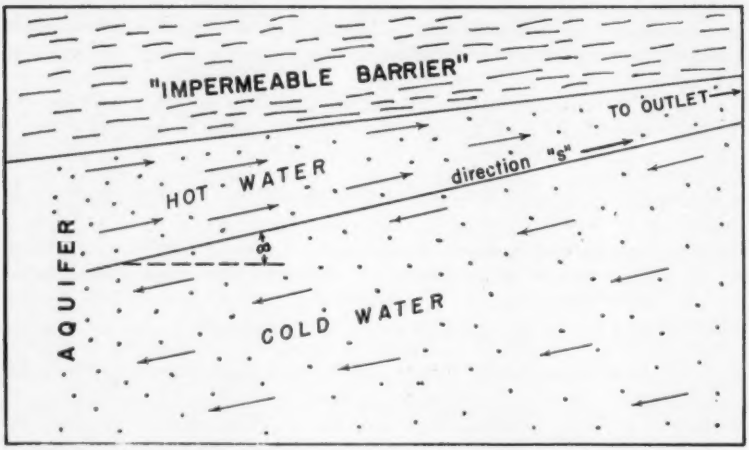

FIG. 1. Diagrammatic cross-section illustrating flow of hot water and cold meteoric water in an aquifer.

of the direction of movement and the slope of the interface may thus be obtained.

Ore deposition is obviously limited to the volume of rock occupied by the ore-bearing fluid under conditions of dynamic equilibrium. Prediction of the boundaries, even crudely, will help analytic thinking in the search for new ore deposits. A hypothetical example will serve to illustrate. Consider a permeable fracture zone striking transverse to irregularly dipping limestone that is overlain by relatively impermeable shale. The permeable zone is limited by the shale on top and by less permeable limestone on either side of the fracture zone. In addition, the hydrothermal zone may be limited by cooler meteoric water on the bottom, except in restricted columns where the hot water is rising through the meteoric water. Utilizing this framework of thought and

the general relations already outlined, it can be seen (Fig. 2) that the hydrothermal zone is thicker near the lower edges of structural terraces and thinner near the upper edges, provided the permeability is constant along the fracture zone. If the permeability varies, the liquid interface is steeper where the permeability is smaller and vice versa.

White and his coworkers (22, 23, 24) have described antimony deposits in Mexico, where these considerations would seem to apply especially well. According to White and Gonzáles (22, p. 141), "The known localization of the ore bodies strongly supports the hypothesis that the antimony-bearing solutions for the most part came up the major faults and fractures until their progress was impeded by the relatively impermeable shale overlying the limestone. The solutions then migrated on up the faults on the limbs of the

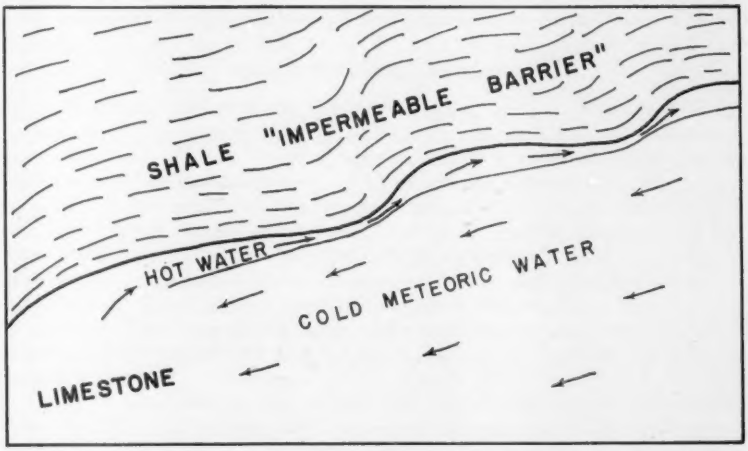

FIG. 2. Diagrammatic cross-section along a fracture zone that is permeable in the limestone.

intersecting anticlines to the anticlinal axes. Most of the migration then took place in the mantos on the anticlinal axes. . . . The upward rake to the southwest of nearly all the fold axes favored a general migration of the solutions to the southwest." From this description, one is led to suspect that meteoric water played an important part, for otherwise no reason is evident for localization directly beneath the shales, and no reason is evident why the axes of synclines were not mineralized, for they were probably as permeable as the anticlines.

In the absence of permeability barriers, the hydrothermal fluid will tend to spread out on top of the normal ground water, and the result may be flat or gently dipping ore bodies without structural control. Under other conditions the rocks may be so impermeable, and the permeable fracture zones so limited in volume, that the rising hydrothermal fluid completely fills the permeable

zones to the exclusion of normal ground water. Some of the deposits in higher stratigraphic horizons in the Terlingua district are probably representative of these conditions. Individual variations, many of which may be classified as variations in the "aquifer," or in structural control, are innumerable, but the general principles should apply to many shallow ore deposits where gravity played an important part in moving the ore-bearing fluid.

The concepts outlined here may be useful in the geologic search for new epithermal ore bodies. Information on "structural control" (which may be regarded as delimiting the aquifer in three dimensions), combined with all obtainable information on mineralization centers, could be correlated with information on the present hydrodynamic situation. The result should be a better knowledge of the limits of the zones in which hydrothermal fluids flowed than could be obtained without hydraulic studies. The chemistry of the wall rocks may also be important, as is pointed out in a later section.

PRECIPITATION OF CINNABAR.

Several factors tending to localize ore deposits have been discussed. The ore tends to be limited to permeable rocks and further restricted to the portion of the permeable rocks that was at some time occupied by the ore-bearing fluids. Parts of the channels traversed by the ore-bearing fluids in the Terlingua district are relatively barren, however, and the concentrations of cinnabar are markedly spotty. This fact leads one to suspect the operation of chemical or physical controls not touched upon in the previous discussion.

In the following discussions, emphasis is on the problems of precipitation from a liquid, although some of the ore may have been deposited from a vapor. Generally speaking, factors that might cause precipitation are decrease in temperature, decrease in pressure, evaporation or condensation, dilution, and wall-rock reactions, including changes in pH. Still other factors may influence precipitation from supersaturated solutions or colloidal solutions.

Decrease in Temperature or Pressure.—The experimental work of Knox (25) and Saukov (15) shows that the solubility of HgS in alkaline sulfide solutions has an inverse relation to temperature; decrease in temperature actually makes the solubility greater. Decrease in pressure, likewise, would have little effect on the alkaline sulfide solutions studied by Knox and Saukov, other than to promote evaporation, which is considered separately in the next section. Furthermore, decrease in pressure fails to explain the distribution of the deposits, which one might expect to be in and above constrictions in the channelways if pressure drop were the main cause of precipitation.

Evaporation and Condensation.—Experiments on the efficacy of evaporation to precipitate mercury sulfide were carried out because Dreyer (6) has emphasized evaporation as a probable cause of precipitation. Solutions of 0.04 molar Na_2S and 2.0 molar Na_2S were saturated with HgS. When these solutions were evaporated by boiling, no precipitation occurred until near dryness, when an orange and yellow precipitate formed. The dry precipitate was readily soluble in a few drops of distilled water. This result is in accordance

with the work of Knox (22), who prepared a complex salt of sodium sulfide and mercury sulfide by evaporation.

The solubility data of Knox (22), reproduced in Table 1, show that the solubility of HgS increases with concentration of Na_2S in a solution and, moreover, increases at a greater rate than the increase in concentration of Na_2S. Only when the solution is made strongly alkaline by the addition of NaOH is a point finally reached where the ratio of HgS to Na_2S decreases with increasing concentration of Na_2S. This means that HgS can be precipitated by evaporation only from the most strongly alkaline solutions studied by Knox. Such extreme alkalinity is so unlikely under the moderating influences of the geologic environment that further discussion is unnecessary.

The effects of evaporation and condensation may be quite different, however, in the presence of a vapor phase containing gases such as CO_2 and H_2S; these gases are so common in hot springs and in volcanic emanations in general that their influence should be considered. In a system composed of both gas and liquid the solubility of HgS in the liquid would be decreased by boiling off

TABLE 1 (after Knox).

Conc. Na_2S mole/liter	HgS dissolved in mole/liter						Ratio HgS/Na_2S, NaOH 7.7N
	In Na_2S solution	In Na_2S solution with added NaOH					
		NaOH 0.5 N	NaOH 1.0 N	NaOH 4.48 N	NaOH 4.67 N	NaOH 7.7 N	
1.015	0.4423	—	0.673	—	—	0.9167	0.903
0.755	0.2878	—	0.485	—	—	—	—
0.50	0.1500	0.2483	0.302	0.435	—	0.4637	0.927
0.25	0.04544	0.1106	0.148	—	0.225	0.2369	0.948
0.10	0.008241	0.03962	0.0563	—	0.0903	0.09634	0.963

H_2S and increased by boiling off CO_2, the latter because loss of CO_2 causes an increase in pH. Condensation would have an effect opposite to that of boiling.

Whether the solubility of HgS would actually increase or decrease when boiling causes a reduction of both gases in the liquid phase is impossible to decide on the basis of present information. If the solubility is increased by evaporation and, conversely, decreased by condensation, precipitation from both the gas and liquid phases could be brought about by increase in pressure or decrease in temperature. Horizontal portions of the channelways, where the temperature may decrease more rapidly than the pressure, might thus be favorable sites for deposition.

Dilution.—Dilution should be effective in precipitating HgS, as shown by the solubility data (22), which are plotted graphically in Figure 3. As an example, suppose that one liter of 1.0 molar Na_2S solution saturated with black HgS is diluted to 0.1 molar. The original solution contains 0.50 mole/liter of HgS and the diluted solution can hold 0.01 mole/liter in solution. But as there are 10 liters of dilute solution (one part of the original solution

together with nine parts of water), that solution contains 0.10 mole of HgS altogether, and 0.40 (0.50 minus 0.10) mole of HgS is precipitated. This means that four-fifths of the dissolved HgS is precipitated as a result of dilution. Although the available solubility data are for solutions that may be considerably more concentrated than natural ore-bearing solutions, the solubility curve, Figure 3, shows that the ratio Na_2S/HgS increases more and more rapidly with increasing dilution—in other words the curvature increases in

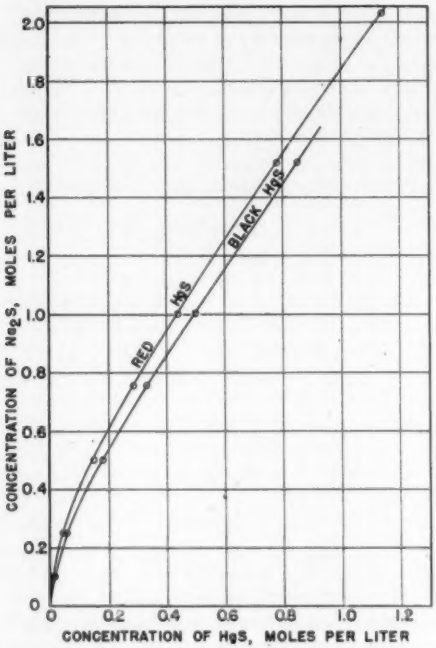

FIG. 3. Variation in solubility of red and black HgS with concentration of Na_2S. The slope of the curve at any point is the ratio Na_2S/HgS. Where the slope increases with decreasing concentration, dilution will cause precipitation. The curve shows that dilution becomes increasingly effective in precipitating HgS as the concentration decreases. Data from Knox.

this direction—and therefore as the concentration decreases, dilution becomes progressively more effective in causing precipitation.

Meteoric water, because of its lower pH and its dissolved oxygen, which may react with sulfur to form acid, would be more effective than distilled water in causing precipitation by dilution.

Experiments to verify the effects of dilution were carried out by diluting 2.0 molar and 0.04 molar solutions of Na_2S saturated with black HgS. Dilution

invariably caused precipitation of black HgS, but the reaction was usually sluggish, and in many cases no precipitate could be detected from the supersaturated or colloidal solutions until several hours had passed. This was true even with dilutions of one part of solution to ten parts or more of distilled water, so long as the dilution was carried out with rapid mixing. (Rapid mixing is easily accomplished by pouring the slightly more dense solution into the lighter distilled water.) After precipitation began, the precipitate accumulated gradually on any available surfaces such as the wall of the test tube, a behavior that is common in supersaturated solutions.

The diluted solutions were tested for colloidal properties by using a strong light beam to look for the Tyndall phenomenon. Under conditions where the solubility was greatly exceeded, colloidal properties were always displayed, though in some cases not for several minutes after the solution was diluted. It was not practicable to make a sharp distinction between supersaturated and colloidal solutions, but the markedly greater solubility of black (metastable) HgS (compared to red HgS) indicates that supersaturation is not negligible. A fuller discussion of this is reserved for the section on supersaturation.

Heating the colloidal or supersaturated solutions to 100° C increased the rate of precipitation. In one experiment, a 2.0 molar Na_2S solution saturated with HgS was diluted one to one with distilled water. No precipitate formed. The solution was then gradually heated to 100° C, and as soon as it got warm a faint black precipitate began to form on the walls of the test tube. The precipitate continued to form for at least 20 minutes after 100° C was reached, accumulating in long streaks along scratches in the tube. As the streaks became heavier they were detached as rods and settled to the bottom, this process being repeated several times along each scratch. Microscopic examination showed the black-appearing precipitate to be largely red crystalline HgS in contrast to the finer grained black HgS obtained in experiments at room temperature.

The solubility data and experiments indicate that dilution is effective in causing precipitation from mercury-bearing solutions. The sluggishness of the reaction and the resultant supersaturation or colloidal dispersion are probably less marked at higher temperature. The nature of the material forming the walls of the channelways may also be important; one would expect clay, with its large surface area, to cause more rapid precipitation from a supersaturated solution than a wall rock like limestone. In attempting to test the catalytic effect of clay in this respect, another chemical effect was noticed, however, which will be discussed in the section on reactions with wall rocks.

The geologic data on the Terlingua deposits help little in evaluating the effectiveness of dilution. One would expect dilution to take place all along the interfaces between the ore-bearing solution and the normal ground water, and the actual distribution of deposits near the top of a permeable limestone is not inconsistent with this expectation, although the almost complete lack of deposits extending downward in the limestone, through which columns of hydrothermal fluid must have risen, appears to eliminate any possibility of explaining the detailed distribution of the deposits solely on this basis.

Reaction with Wall Rocks.—As previously stated, a large part of the ore is near the intersections of steep fractures with the gently dipping contact of the Devils River limestone with the overlying Grayson formation, which is composed in large part of calcareous clay and is so poorly consolidated that it disintegrates in water. Some of this ore is in the limestone, but a large part is in the clay, where the cinnabar commonly occurs in bands parallel with the bedding of the formation. The detailed association of cinnabar with clay is noticeable also where clay has slumped into fractures enlarged by solution in the limestone; in places cinnabar has been precipitated selectively in pods of clay several tens of feet below the upper contact of the limestone.

The detailed association of much of the ore with clay of the Grayson formation suggests that the clay, by some physical or chemical reaction, causes precipitation. Preliminary experiments showed that when a piece of clay from the Grayson was put into an Na_2S solution saturated with HgS, a precipitate of HgS sometimes formed on the clay. Results were unpredictable, however, as though the clay reacted chemically with the solution but that supersaturation instead of precipitation occurred in some cases. Two ways in which clay might be effective in aiding precipitation are suggested: (1) The clay, because of its large surface area, may catalyze precipitation from supersaturated solution. (2) Clay may act as a buffer and tend to neutralize alkaline solutions by exchange of metal ions in the solution for hydrogen ions in the clay, thus increasing the hydrogen-ion concentration in the solution and lowering the pH.

Differential thermal analyses were made of several clay specimens from different parts of the Terlingua district. The results indicate that illite is the main constituent of the unaltered clay. Kaolinite is also present in at least one of the specimens, and calcite is a subordinate constituent of all the specimens examined.

The buffering action of the clay was tested experimentally, and it was found that a small amount of clay is capable of appreciably lowering the pH of a relatively large volume of alkaline solution. Three grams of clay stirred into 100 cc of a 0.01 molar solution of Na_2S causes the pH of the solution to drop quickly from 11.7 to 11.5. More dilute solutions of Na_2S or NaOH undergo a greater reduction of pH under similar conditions.

To eliminate sources of error in these experiments, several precautions were necessary. The pH of sodium sulfide solutions is changed by oxidation or absorption of carbon dioxide from the atmosphere. Control solutions, to which no clay was added, maintained a constant pH during the time interval of 5 or 10 minutes necessary for adding the clay to the test solutions and measuring the pH. The control solutions continued constant in pH for at least half an hour, although all the solutions underwent a reduction in pH when left open to the atmosphere for many hours. Jenny and his colleagues (26) have pointed out an error in the measurement of pH by means of glass electrodes in suspensions of clay. They have shown that the liquid junction potential operates in the direction of making the pH of suspensions appear lower than the correct value, and the error may be very large if the electrodes are pushed into a paste consisting of clay and water. To check for this error, the solu-

tions were allowed to settle or were filtered after mixing with clay. It was found that the error was small so long as the electrodes were not pushed into the settled mud. The results were also verified with indicator papers.

The buffering action of the clay, although appreciable, can hardly be the entire explanation of the detailed association of much of the ore with clay. A gram of clay, in order to precipitate 10^{-2} grams of mercury and thus form 1.0 percent ore, would have to extract all the mercury from 10^{5} grams of saturated solution, assuming the solution contains the minimum concentration of 10^{-5} percent mercury. This seems hardly possible on the basis of pH change alone, particularly in view of the limited amount and the low permeability of the clay. It would seem that the principal possibilities left to explain the selective deposition of the ore in clay are: (1) The ore-bearing fluid was out of chemical equilibrium and supersaturated at the points of deposition; clay acted as a catalyst; or (2) the ore-bearing fluid was in part colloidal at the points of deposition.

Supersaturation.—A prominent characteristic of the Terlingua quicksilver deposits, and for that matter of many other epithermal deposits, is the passage from rich ore to barren rock and back to rich ore within a few feet or a few tens of feet along ore-bearing structures. In many places this detailed concentration of the ore in restricted pockets cannot be explained by differences in permeability or structure, or by any reasonable hydrodynamic relations, although these are sufficient to explain the general distribution. It is just as difficult to explain the spotty distribution by any chemical means under conditions of equilibrium. By the principle of Le Chatelier, if the conditions of a system are changed, the equilibrium will shift in such a direction as to tend to restore the original conditions. A simple example is a fluid from which something is precipitated because of falling temperature; precipitation releases heat and the process soon stops unless heat is continuously carried away. How, in an ore deposit, can heat have been continually lost for a long time at one place in the channel and not from an immediately adjacent place? If dilution is responsible for precipitation of the Terlingua ores, how could it have occurred here and there without any evident structural or hydrodynamic control? If reactions with the wall rock are responsible, why were the reactions restricted to certain places in the same rock? The geologic conditions require a mechanism to explain discontinuous precipitation under continuous conditions of change.

It seems to the writer that this problem has only one answer: equilibrium was not maintained at all points. Disequilibrium reactions are, within limits, free from the restrictions of Le Chatelier's principle, and localized deposition from supersaturated solutions is possible. Supersaturation and other phenomena of metastability are probably more common than is generally realized. Water heated as much as 3° C above its normal boiling point has been observed in thermal springs (12, 13). Such water may be thought of as supersaturated with its own vapor. At the other extreme, water drops may be cooled to − 38° C without formation of ice (27), and Heverly (28) found the spontaneous freezing point to be independent of agitation, pressure, dissolved NaCl up to one percent, or cooling rate. The supercooling was found to depend

upon the diameter of the droplets: the smaller the droplets, the lower the spontaneous freezing point. It is well known, as Kolthoff (29) has emphasized, that a supersaturated solution of zinc sulfide is obtained in ordinary analytical procedure when the Group II metals are precipitated in slightly acid solution. It is also well known that small particles are more soluble than large particles, and therefore a solution in equilibrium with small crystals is supersaturated with respect to large crystals. Verhoogen (30) treated the quantitative problem theoretically, but his calculations do not seem to be strictly applicable to crystals, which have flat faces instead of curved surfaces.

The solubility data of Knox (25) show clearly that the black metastable form of HgS is markedly more soluble than cinnabar, the stable form. This

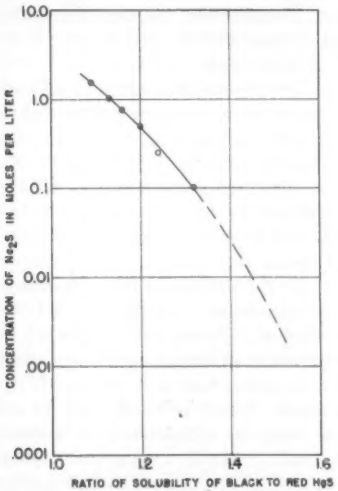

FIG. 4. Ratio of solubility of black (metastable) HgS to red HgS in Na_2S solutions. Data from Knox. The curve shows that saturated solutions of black HgS are supersaturated with respect to the stable red form of HgS, and the degree of supersaturation increases with decreasing concentration of the solutions.

is shown in Figures 3 and 4. Figure 4 shows that the degree of supersaturation increases with decreasing concentration of the solutions. By extrapolation, dilute ore-bearing solutions, if saturated with black HgS, are probably at least 50 percent oversaturated with respect to red HgS. The writer heated 0.1 molar Na_2S solutions saturated with black HgS (32 percent supersaturated with respect to red HgS) to 100° C without obtaining any precipitate, even though heating decreases the solubility of HgS. No evidence of colloidal properties could be detected in these solutions by examination in a strong light beam. Even when seeded with cinnabar crystals the hot solution persisted in a state of supersaturation. After about half an hour at 100° C the solution showed a faint Tyndall effect when tested with the beam of light.

Precipitation from supersaturated solutions might be brought about simply by slow continuous approach to equilibrium, by rapid precipitation in the presence of seed crystals or a catalyst, or by rapid spontaneous crystallization starting at a critical degree of supersaturation. Clay may react with the solutions to increase the degree of supersaturation slightly, but possibly its main role is to catalyze precipitation because of its large surface area. Continuous changes in physico-chemical conditions could thus result in sporadic precipitation.

Systematic experimental data are badly needed, particularly at temperatures above 100° C and for very dilute solutions, which might be expected to be more stable when supersaturated than the solutions tested in the present investigation. Concomitant experiments are needed on colloidal HgS solutions.

Colloidal Deposition.—Pollock (31) emphasized the view that HgS was carried as a colloid in the final stages of transportation and deposited from colloidal solution. He suggested that colloidal HgS solutions could result from rapid dilution or neutralization of an alkaline sulphide solution, and he introduced experimental evidence to show that colloidal HgS solutions may be stable at least up to 100° C (confirmed by the present writer) and in the presence of electrolytes. Quicksilver deposits consisting of cinnabar microscopically disseminated through opal and chalcedony were considered to be further evidence of colloidal transport, and silica was regarded as a protective colloid.

Siliceous quicksilver ore is not found in any quantity in the Terlingua district, and most of the cinnabar is relatively coarse. There is thus less suggestion of deposition from colloidal solutions in this district than in some others.

CONCLUSION.

An adequate hypothesis to explain the transportation and deposition of quicksilver ores in the Terlingua district in accord with Krauskopf's findings and with the geology can be outlined. Some distance below the zone of deposition, steam and other gases carried mercury vapor and volatile mercury chloride along with sulfur and hydrogen sulfide. As Krauskopf has pointed out, this is a reasonable explanation for the separation of cinnabar deposits from most other sulfide ores. At shallower depth most of the gas condensed. If the fluid was originally acid, reaction with limestone resulted in near-neutral solutions, but if it was originally alkaline it probably remained on the alkaline side of neutral, though transfer of carbon dioxide from the gas phase to the liquid phase would tend to reduce the pH. In the zone of deposition, at a representative depth of 900 feet, the fluid was probably predominantly liquid, had a pressure of about 30 atmospheres, and a temperature of about 200° C. It was probably a sodium chloride water containing at least 0.1 mole/liter of sulfur, at least 10^{-5} percent mercury dissolved as the complex sulfide, and small amounts of several other elements. The hydrothermal fluid was restricted to permeable zones and further limited by hydrodynamic conditions involving normal ground water; for this reason the hydrothermal fluid rose and

migrated along the tops of aquifers. Intermixture and dilution by normal ground water resulted in supersaturated and possibly colloidal solutions, from which masses of cinnabar precipitated sporadically, aided in places by clay wall rock. Native mercury, some of the cinnabar, and possibly some of the mercury chlorides were deposited from vapor that accompanied the hydrothermal solution.

The probability of deposition from a liquid phase has been emphasized because of the extensive replacement of calcite by cinnabar in the Terlingua district and the seeming impossibility of calcite being carried away in a vapor phase. Under the prevailing conditions an alkaline sulfide solution is the only type of equilibrium solution known to be capable of carrying enough mercury. The possibility remains that replacement of calcite could be accomplished by an intimate mixture of gas and liquid phases, with mercury transported mainly in the gas phase. It is also conceivable that mercury may be carried in solution by a mechanism as yet unknown; the conflicting data pointed out by Krauskopf on the possibility of transportation as a sulpho-mercuric acid emphasizes this possibility.

In the search for new deposits, closer analysis of hydrodynamic conditions is desirable. Under favorable circumstances it may be possible to predict more closely what portion of the permeable rocks is most favorable. If supersaturation is as important as here suggested, an investigation of precipitation from supersaturated solutions might yield information of aid in the search for new deposits. There may be a tendency for supersaturated solutions to form deposits with a systematic spacing; and the influence of various wall rocks may be important.

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CERTAIN TERMS OF MINING GEOLOGY AS DEFINED AND USED.[1]

HARRISON SCHMITT.

ABSTRACT.

A limited number of terms of petrology and mineral deposits, both descriptive and genetic in nature, are reviewed and discussed. The writer believes that there is still too much careless and subjective use of terms. This in part arises from the currently sharp separation of practice from theory. The terms stock and batholith are too often used subjectively. Terms defining changes in rocks seem to need clearer definition. The term contact metamorphism is particularly troublesome. In the genetic category hydrothermal and pneumatolytic appear to need clarification.

INTRODUCTION.

MANY have experienced the confusion generated in debate or formal exposition when terms are not accurately defined. R. A. Daly says, "Someone has said that discussions generally end where they should have begun—with the definition of terms." Augustus Locke used to say before a discussion, "Let's first define our terms." We mining geologists are perhaps no more at fault than other scientific groups, but the great emphasis on application as contrasted with theory has led to uncritical habits. We have unconsciously developed a jargon that may be understood at the mines, but in technical expression leads to an unnecessary lack of clearness. Those who criticize manuscripts on mining geology find otherwise important contributions marred by the misuse and subjective use of terms. T. B. Nolan[3] states—"The profession . . . need(s) to use words accurately if we are to ask people to believe we think clearly and accurately."

Economic geologists have been the target of serious criticism this past decade. An eminent scientist in another field has said that in the field of theory at least we appear to have been developing a pseudo-science. Geophysicists (in the general sense) and geochemists have asserted that if we do not fully utilize basic science they will take us over. They may have made a fair start at this; at least they are forcing us to a reappraisal. We are faced with the need of building our science on a better and more logical base with the clarification and improvement of terminology as a first step.

Although there appears to be a need for a new, complete and carefully thought out glossary of terms for mining geology, this paper can consider only

[1] This paper was presented to a joint session of the Society of Economic Geologists and the Am. Inst. of Min. & Metall. Engrs., New York, Feb. 20, 1952.

For a recent glossary see McKinstry (7, p. 63–659) [2] and for useful general definitions see Bateman (1).

[2] Numbers in parentheses refer to References at end of paper.

[3] Personal communication.

a few that seem especially troublesome or often misused, and suggestions are offered for debate with the hope that in time opinion will clarify on preferred usage. Our first aim should be to sharpen the meaning of terms where that can be done without greatly violating current usage.

The most useful and enduring terms are those whose meaning is objective, that is, divorced from controversial and unproved hypothetical or genetic implications. Except in delimited discussion we should avoid the subjective. A few terms will be discussed below under the heading of (A) relevant petrologic terms, (B) terms pertaining particularly to post-primary changes in rocks and (C) mineral deposit and genetic terms.

RELEVANT PETROLOGIC TERMS.

1. Stock, Plug, Neck, Cupola and Batholith.[4]—In the igneous rock category stock is one of the terms of particular interest to mining geology. In this country B. S. Butler and W. H. Emmons, particularly, have indicated at least spatial if not genetic relationship between many stocks and ore deposits.

Daly has given a valuable discussion of igneous rock bodies with a definition of terms (2, p. 74–136). Apparently batholith, stock and cupola belong in the same category. There is no sharp separation between batholith and stock; they are both grouped in the subjacent class by Daly who explains that this implies *a lack of knowledge only* of their shape in depth although their masses are often observed to increase in depth. All other intrusive bodies are classed as injected. By observation some so-called stocks and/or cupolas are injected forms, that is, they have been intruded under pressure.

Apparently a cupola can be part of a stock but a stock is not necessarily a cupola. Grout following others says that stocks, by definition, are small batholiths with areas not greater than about 20 square miles. In the case of batholith and stock, Daly infers that the concept of indefinite enlargement in depth is a subjective one and should be abandoned. The definition is negative in character. In other words, the batholith and stock are of unknown extension and shape in depth. Many of the early Archean so-called batholiths are known to be floored and, following Daly, belong to the class of injections. The late Archean granite masses, however, have increasing bulk in depth so far as has been observed.

So far so good, but when we come to apply the above terms and concepts we become careless. Data of critical significance are too often not available which tends to encourage subjective assertion when we should objectively admit ignorance. Thus, in a given ore district, adjacent, coarse-grained, large igneous masses are often revealed in horizontal cross-section only. They are usually called stocks without qualification yet later through mining development may be shown to be masses belonging to other classifications. Further, if no batholith is visibly associated with an ore district we boldly postulate one even if in the province concerned contemporaneous batholiths are unknown. Ore deposits apparently are formed in many different ways. Many do not appear to be even spatially related to stocks, cupolas or to batholiths.

[4] See appendix for definitions.

We should more often use the generic and non-committal terms igneous mass, pluton and chonolith.

2. Terms Used in the Field of Shallow Volcanism.—The terms vent, pipe and diatreme [5] refer to volcanic conduits without commitment as to rock content. On the other hand, neck and plug [5] seem to refer to the filling without commitment as to character of the filling, but they imply a conduit. The above terms are used with modifiers such as breccia-pipe, lava-plug, etc. for more complete description. By definition a diatreme is a breccia-filled vertical pipe which had been opened by pure explosion (or gas erosion ? author), but a volcanic vent or pipe presumably usually has the same origin. Breccia pipes, as observed at Cananea, Sonora, Mexico, do not necessarily communicate directly upward with the surface. These should be called pseudo-pipes. Their origin seems mysterious and may not be closely connected with volcanism, although some may be the result of explosive release of gas pressure downward or sidewise.

Since the "epithermal" or "Tertiary type" of ore deposits is often associated with shallow volcanism it is important to consider, and, if possible label, the associated igneous forms commonly encountered. These include indogenous domes with their funnel or ethmolith-like bottoms, and volcanic necks filled with funnel-shaped breccia and lava.

TERMS PERTAINING PARTICULARLY TO POST-PRIMARY CHANGES IN ROCKS.

Terms defining changes in rocks are numerous and are generally clear and objective. Many are closely descriptive, that is, the name of the chief mineral is used for the base of the word. Useful generic terms include tactite, skarn, and Lovering's recent term argillization. Propylitization varies in meaning with different students (Schmitt 8, p. 194). One may well ask if it falls under mineralization, metamorphism or alteration. The Europeans, in some cases at least, apply the term to regional chloritization.

The term metamorphism appears to be adequately defined by Harker (4a, p. 1–27, Chaps. I, II).

Turner and Verhoogen (10, p. 368) define it concisely as follows:

> According to general usage of the term *metamorphism* refers to the mineralogical and structural adjustment of solid rocks to physical or chemical conditions which have been imposed at depths below the surface zones of weathering and cementation and which differ from the conditions under which the rocks in question originated.

Lindgren (6, p. 91) reserves metamorphism "for the processes which result in partial or complete crystallization or recrystallization of solid masses of rocks." "The composition of the rock as a whole, while remaining fairly constant undoubtedly has a tendency to change." These statements seem vague to this writer. They equally well define certain phases of metasomatism and especially alteration. Lindgren would seem to have metamorphism partially overlap metasomatism and greatly overlap alteration. Particularly, we do not seem to have clearly defined a field for the term alteration. Lindgren

[5] See appendix for definitions.

states (8, p. 92): "Alteration . . . (is) synonymous with certain phases of partial metasomatism of rocks."

Turner's and Verhoogen's definition of metamorphism seems sound with alteration possibly reserved as a special term for low grade metamorphism. However, also see McKinstry (7, p. 632) whose statement, "typically brought about by *hydrothermal solutions*," appears subjective.

The process term contact metamorphism from the historical point of view of the European petrologists (4a, p. 21) should be used only to denote changes at or even far distant from an igneous contact *without* appreciable addition of substance. For far distant heat metamorphism, however, Harker recommends the use of thermal metamorphism. Around the mines and when talking to the engineers and operators there is perhaps no objection to the employment of this term in the current inaccurate way; that is, to denote ore forming and additive processes near an igneous contact, but when serious writing is done the more precise compound terms available should be used. These utilize metamorphism and metasomatism as root words, the latter only signifying appreciable addition of substance, with modifying words and prefixes such as contact, pyro, igneous, thermal, dynamic, hydrothermal, pneumatolytic or fluidic added in an objective sense.

The terms hornfels and hornstone according to Kemp are nearly synonymous (5, p. 126–7). Grout would prefer to reserve hornstone to flints and cherts. Possibly hornstone should be reserved to flints and cherts and since hornfels usually refers to (and can be reserved for) rocks with macroscopic metacrysts there may be a place for a term for the dense, glass-hard, aphanitic, baked shales. For this porcellanite has been proposed (4, p. 371; 8, p. 135, but see appendix). Similar rock has often been inaccurately called silicified limestone. Genetically it is important to make a distinction since the latter usage implies imported silica. Jasperoid is available for masses of imported silica.

MINERAL DEPOSIT AND GENETIC TERMS.

Etymologically viewed the term mineral deposit could include any mass of minerals including igneous rocks, etc., but usage restricts the term to an economic or potentially economic mass of minerals. The scope of the term is rapidly widening as an increasing variety of minerals becomes of commercial interest. Even certain igneous rock aggregates of economic value probably may be included.

The related process term mineralization, which broadly viewed could likewise include the formation of all minerals, has been restricted to the formation of those of economic or potentially economic interest or related to or indicative of these (6, p. 92). This term in mining geology often seems either too loosely or too narrowly applied. Thus, pre-mineralization or post-mineralization is often used when the pre-ore or post-ore stage of mineralization is meant. Obviously the genetically related wall rock alteration belongs to the whole broad mineralization period which may precede and/or follow the ore stage.

Recently it was noted that in the Carlsbad district the potash ore beds were said to be mineralized ground and when formed were mineralized. Since these deposits must surely be called mineral deposits the above seems logical if unusual usage.

Apparently the term mineralized is commonly used as both a verb and adjective. T. B. Nolan, in a personal communication, deplores the use of "words designating 'process' for the 'product' of the process." The variations of the words mineralized and mineralization, however, used as verb, adjective and noun are too firmly intrenched to change and, indeed, seem to the writer to function usefully.

A term is needed that labels economically potential ore as well as ore. Metallization will do in many instances but will not serve for non-metallic deposits. For the time being ore-mineralization whether metallic or non-metallic may serve for the ore or potentially ore stage.

The terms hypogene and supergene have been exceedingly useful but some now think that minerals formed in the shallow zone, as in the "epithermal"-hot spring environment, are determined by a mixed hypogene and supergene environment. Here there may be a place for such a term as *mesogene* if, indeed, this term has not already been suggested.

The terms hydrothermal and pneumatolytic [5] are often loosely used. Possibly hydrothermal should be restricted to processes occurring below the critical point of water or the aqueous solution involved, and pneumatolytic to those occurring above, but, since in the present state of our knowledge we cannot usually fix the critical point when the deposit was formed, an alternative suggestion is to use hydrothermal for *any* aqueous solution or fluid above or below this point. We can then use, as modifying terms, liquid, gaseous, pneumatolytic, dense or tenuous. The term fluid should be employed when the accurate application of the terms liquid or gas is uncertain.

In the field current use of the term geophysics has been confusing. This term should retain its original meaning, "the physics of the Earth." The application of geophysical methods should be differentiated from the parent word; thus, mining geophysics, petroleum geophysics, field or applied geophysics, etc.

Geochemistry seems too grandiose a term for the mere application of systematic sampling and quantitative chemical analysis to ore finding. We should at least say field or applied geochemistry or soil and plant sampling. It would be better to invent a new term. Trace element prospecting may be all right.

The writer is greatly indebted to Augustus Locke, Thomas L. Lovering and Thomas B. Nolan for their careful criticism of this paper.

APPENDIX.

Suggested Definitions and Discussion of Terms Considered in the Paper.

Alteration . . . . . Apparently now reserved for low grade metamorphism, but overlaps mineralization and may be considered related to ore mineralization. This latter inference, however, would be subjective in many cases.

Batholith . . . . . An igneous mass greater than 20 square miles in area. Unless the rock is known to extend a minimum of several miles in depth the term should be written with a question mark, (?).

Cupola . . . . . An upward restricted projection or knob-like form of a batholith or stock that enlarges in depth. Unless enlargement in depth and relationship to a stock or batholith is known this should be written with a (?) mark.

Diatreme . . . . . A pipe opened by pure explosion but later filled in with breccia. This term may be of restricted use because of the difficulty of proving an origin by pure explosion. The result of catastrophic prolonged (secular) gas erosion of vents would presumably follow this definition. In any case a diatreme would seem to be simply a filled-in volcanic vent, i.e., a breccia pipe.

Dome . . . . . A central protrusion of lava in a crater (2, p. 149–153).

Ethmolith . . . . . A plutonic mass of igneous rock that narrows downward (funnel-like).

Geophysics . . . . . The physics of the earth.

Hornfels . . . . . Rosenbush designates this term for rocks totally reconstructed (Harker, 4a, p. 23), but Harker later (4a, p. 39) says the word has lost precise meaning.

Hornstone . . . . . A general term for cherts and flints (after Grout).

Hydrothermal . . . . . That environment which includes water at higher than room temperature.

Jasperoid . . . . . Dense aphanitic siliceous rocks originating largely through the introduction of silica.

Mesogene . . . . . A term proposed for the environment of intermingled hypogene and supergene fluids.

Metamorphism . . . . . Post-primary changes induced in a body of rock by a change in environment. No appreciable change in composition (overlaps mineralization?). (Also see Turner and Verhoogen, 10, p. 368.)

Metasomatism . . . . . Metamorphism with an appreciable change in composition (4a, p. 2). (Overlaps mineralization ?)

Mineral deposit . . . . . A mass of minerals or of a single mineral of economic or of potentially economic value. This definition is determined by usage but may be too narrow.

Mineralization . . . . . (1) The process of or (2) the result of an induced change in a body of rock that results in (a) a mass of economic value, (b) a mass of potential economic value or (c) masses of rock that are related to (a) and (b) in origin. Usage appears often unduly restricted as that of the term mineral deposit.

Mining geophysics . . . . . The application of special geophysical methods to ore finding.

Neck . . . . . A vent or vertical pipe filled with lava.

Pipe . . . . . A tube-like or pipe-like form of vent.

Plug . . . . . A synonym for neck.

Pneumatolytic . . . . . A high-temperature "gaseous" environment, but see Shand (9a, p. 159). Shand thinks the term has lost precise meaning through variable use.

Porcellanite . . . . . Porcelainized dense aphanitic shales and limy shales (no silica introduced). This term may have been pre-empted for silicified volanic rock, but this is also called vitrophyr. Also see Kemp (5, p. 245).

Stock * . . . . . (1) A batholith smaller than 20 square miles, (2) a cupola. In either case a question mark (?) should be used unless the depth is known to be at least several miles.

Vent . . . . . A general term for a volcanic opening that penetrates the depths.

SILVER CITY, NEW MEXICO,
September 1, 1953.

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* Following Daly, Grout and Emmons.

COMPOSITION OF VEIN-FORMING FLUIDS FROM INCLUSION DATA.[1]

F. GORDON SMITH.

ABSTRACT.

Data from study of inclusions in vein minerals indicate that there are two main classes of solutions of crystallization: one is aqueous, with either a high salt content or a high carbon dioxide content, and the other is apparently siliceous, but with some water content. Both types fill inclusions to such a degree that the solutions at the time of crystallization must have had liquid, not gaseous, solvent properties.

FOREWORD.

ABOUT four years ago, a study of fluid inclusions in hydrothermal minerals was started at the University of Toronto. Electronic apparatus was developed to detect and analyse decrepitation due to filling of multiphase fluid inclusions by the liquid phase. Use of this technique led to the study of decrepitation caused by other types of inclusions such as crystalline solids. The results suggested that decrepitation analysis might lead to useful methods for determining the temperature and pressure of formation of minerals. Consequently, the prior data on inclusions was assembled and critically reviewed (1).[2] This body of work (about 500 papers and monographs) was found to give a surprisingly consistent picture of the composition of the fluids responsible for formation of vein minerals. The conclusions from the historical survey, together with microscopic data recently obtained at the University of Toronto, are here summarized.

As a general rule, minerals grow quite imperfectly and include within themselves a surprising assortment of substances. While this fact is a hindrance to the chemist interested in determining the composition of minerals, it is of great aid to the geochemist interested in determining the conditions during crystallization of minerals. Most of the reliable information on the composition and density of solutions that deposit vein minerals has been derived from studies of liquid inclusions, small though they may be. (Sorby, the first systematic investigator of inclusions, evidently had some trouble convincing skeptics of this branch of microscopic petrography, because he took some pains to point out that there is no necessary relation between the importance of a fact and the size of the object that affords the fact (2).)

[1] Presented as a part of the panel discussion on "Nature and origin of the ore-forming fluids," Los Angeles Meeting, Society of Economic Geologists and A.I.M.E., Feb. 1953.

[2] Numbers in parentheses refer to References at end of paper.

Substances included within minerals at the time of crystallization (that is, primary inclusions) may be grouped in several ways, such as:

1) the continuous liquid solvent, trapped in various kinds of gross imperfections of growing faces, and in interlineal spaces;
2) discontinuous immiscible fluids, droplets or bubbles of which adhered to growing faces;
3) crystalline solids formerly suspended in the solvent but which adhered to growing faces;
4) crystalline solids that nucleated on growing faces;
5) neighboring crystals that were enveloped by growing faces.

In all investigations of primary inclusions in minerals, the possibility of later changes must be kept in mind. In the first place it is not a simple matter to prove that any one set of inclusions is primary, although the secondary nature of some sets may be established. Also, there is still a controversy over whether or not all liquid inclusions leak in thin section preparations (3, 4, 5). There is somewhat more agreement than solid diffusion in transparent minerals is either impossible or very slow except near their melting temperatures, and therefore need not be considered in those minerals deposited at very much lower temperatures from complex solutions. Taking all the known facts into consideration, it is reasonable to adopt the working hypothesis that most primary inclusions in minerals have not changed in total composition since the time of crystallization of the host minerals.

The types of solutions from which minerals are formed in veins within the earth appear to be only two in number: aqueous saline solutions and hydrous silicate melts, with the further possibility that the first type may have two varieties, one with a high salt content and the other with a high carbon dioxide content. This generalization is based on a large number of investigations of inclusions in many species of minerals.

The principal immiscible phases noted in inclusions when examined at room temperature (in order of frequency of observation) are:

A—In the aqueous type:
1) liquid water (solution),
2) vapor bubble,
3) liquid carbon dioxide,
4) cubical salt crystals,
5) petroleum.

B—In the silicate type:
1) intergrowth of crystals (or glass),
2) liquid water,
3) vapor bubble.

The degree of filling of fluid inclusions by the condensed phases is important in determining whether the fluid had the properties of a liquid or of a gas at elevated temperatures. This was discussed exhaustively in a recent issue of ECONOMIC GEOLOGY (6), the conclusions being that if a fluid has a density

greater than its critical density, it has the properties of a liquid, and if less than its critical density, it has the properties of a gas. Two other facts are relevant: 1) the density of water and aqueous saline solutions under normal geothermobaric conditions within the crust of the earth is greater than the critical density (from P-V-T data and probable geothermobar data), which was discussed in the aforementioned paper, and 2) the density of primary aqueous fluid inclusions in minerals deposited within the earth also is greater than the critical density (from direct observations). Therefore, it is almost certain that aqueous solutions within the earth generally have the properties of the liquid state, no matter how high the temperature. While we know that mixtures of steam and other gases may occur under exceptional conditions of high temperature and low pressure, there is as yet *no recorded evidence from inclusions* to suggest that such mixtures of gases are agents in the formation of mineral deposits, especially any type of economic mineral deposit. With regard to the other principal type of inclusion, apparently composed of siliceous matter and some water, the data are consistent in showing such a high degree of filling that undoubtedly the original complex solutions must have been in the liquid state. Therefore, the facts provided by inclusions discount the importance (and suggest the non-existence) of pneumatolysis as a process of formation of the normal mineral deposits.

While there is a considerable degree of certainty that vein-forming fluids within the earth have liquid-like solvent properties, there is less certainty about their exact compositions, due to the relatively small volume of the material in mineral inclusions. However, there is fairly good agreement in the literature that the aqueous solution type has a high salinity, usually between 5 and 20 percent by weight (7). In many examples the presence of cubical salt crystals in the liquid phase brings the calculated salt content at saturation to about 30 percent. Chloride, sulphate, and carbonates of sodium, potassium, and calcium are the chief salts found by chemical analyses. It is proposed that solutions of this type be designated as *hydrosaline*.

The high salinity of the solutions that deposit vein minerals must be included in any realistic theory of ore deposition. Possible principal sources of such hydrosaline solutions are:

1) Magmatic differentiation (= juvenile water);
2) Decomposition of hydrous minerals at all stages of thermal metamorphism of many types of rocks (= resurgent water);
3) Diagenesis of sediments (= connate water).

No facts appear to have been established for distinguishing hydrosaline solutions derived from each of the above processes (with or without admixture with meteoric water), but there are reasons for belief that the problem is solvable. For example, methods based on trace elements and isotopic fractionation could be employed. However, before the facts are established, any theory that supposes a strictly juvenile origin for aqueous vein-forming solutions is based on speculation.

Liquid carbon dioxide has been observed in so many inclusions that we must conclude that it is one of the important components of some vein-forming

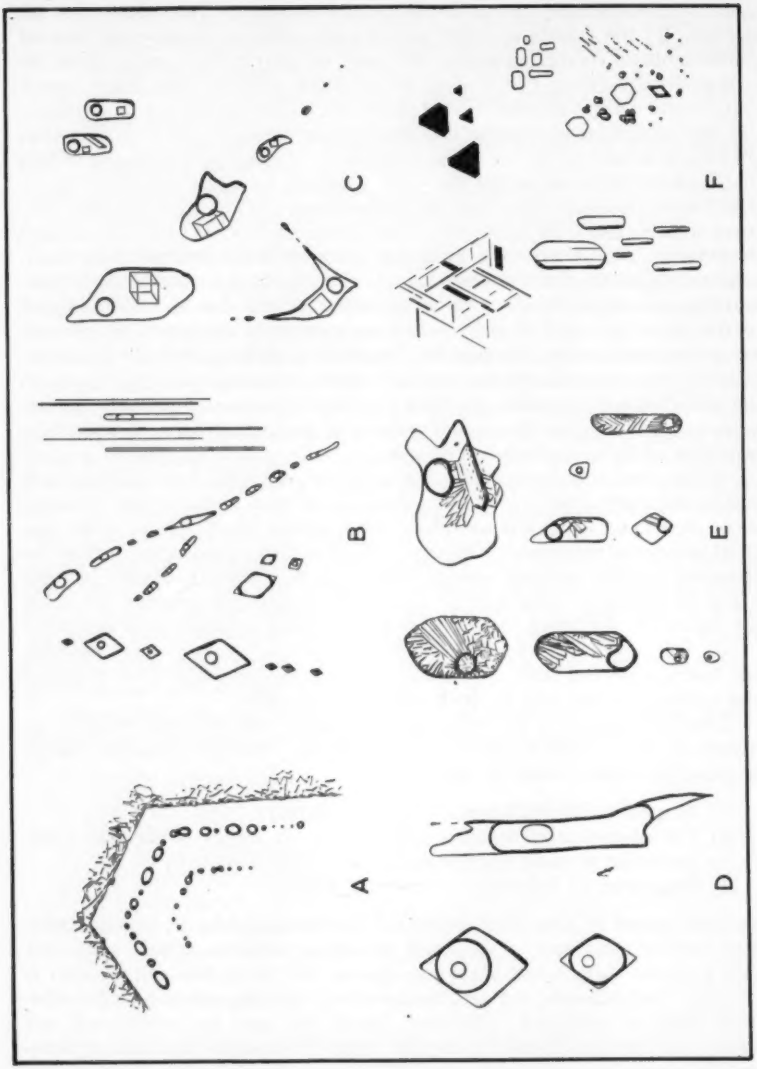

FIG. 1. Description on opposite page.

solutions. Most of the occurrences are in pegmatite minerals (although whether the inclusions are primary or secondary is not yet fully established) and in quartz veins in highly metamorphosed regions. Apparently there is no record of observations of salt crystals along with saline solution and liquid carbon dioxide, which suggests that this type of solution may have a lower salinity than the normal hydrosaline solutions. Since the physics and chemistry of water–carbon dioxide mixtures and solutions are as yet not even explored, speculations on the origin and properties of such solutions at this time would have no value. Tentatively it is proposed to consider solutions rich in water and carbon dioxide as a distinct type, with the designation *hydrocarbonic*.

Petroleum and bituminous materials occasionally have been reported in hydrosaline inclusions. This relation suggests a connate or resurgent origin for some solutions. The ratio of oily materials to water in the inclusions is always variable in any one mineral, and it has usually been assumed that the two liquids were immiscible at the time of crystallization of the host mineral. Therefore there is no immediate use in employing a new descriptive term for this type of liquid mixture.

The composition of the class of inclusions consisting of an intergrowth of crystals, a small amount of liquid, and a small bubble, is not known. The fact that inclusions of this sort have been observed in a considerable number of pegmatitic and contact–metasomatic silicate minerals suggests the working hypothesis that they represent the late silicate fraction of magmatic crystallization. On this basis they may be termed *hydrosilicate*. This type of inclusion has not been observed very often, perhaps because most pegmatitic minerals contain such a vast number of secondary inclusions of several sorts that the few primary inclusions may not be noticed. However, they occur abundantly and often of large size in occasional drusy crystals.

The presence of hydrosilicate inclusions in pegmatitic minerals is not an anomalous fact. According to well developed theories which have considerable support from syntheses, a cooling and crystallizing complex magma will finally produce a silicate liquid enriched in water and other volatiles in addition to many other rare components. This hydrosilicate liquid is responsible for the formation of (at least) the earlier stages of pegmatites. However, it has not been realized in general that physical representatives of the solutions are still permanently sealed in the minerals, and can be observed with little more effort than usually expended in petrographic research. A large body of

FIG. 1. Several types of primary inclusions in minerals as they appear under the microscope at room temperature. A—Gas inclusions in growth bands in phenocrysts of lava. B—Two-phase aqueous inclusions in vein minerals, arranged in growth bands, in interlineal bands perpendicular to growth bands, and also randomly distributed. The gas bubble disappears by shrinkage on heating, usually at 100–200° C. C—Three-phase hydrosaline inclusions. D—Three-phase hydrocarbonic inclusions. The smaller bubble (gas) disappears by shrinkage or expansion below 31° C, and the large bubble (liquid carbon dioxide) disappears by shrinkage or expansion at a very much higher temperature, sometimes about 300° C. E—Multiphase hydrosilicate (?) inclusions in pegmatitic and contact metasomatic silicates. F—Crystalline solid inclusions, oriented and unoriented.

factual data must still be obtained before the importance of hydrosilicate solutions in vein formation can be determined. Data recently obtained at the University of Toronto suggest that both early and later (complex) stages of pegmatite formation, and also the silicate stage of contact metasomatism, are due to hydrosilicate solutions.

Whether 1) there is a continuous change from hydrosilicate to hydrosaline solutions, or 2) there is a temperature overlap of the two kinds with immiscible relations, is still controversial. Two independent series of synthesis experiments (Friedman and Smith, 8, 9) have demonstrated an immiscibility possibility, but the variations of composition may not have included the natural conditions. The problem may be resolved by study of inclusions in late pegmatitic and related vein minerals and by further study of miscibility of hydrosaline and hydrosilicate solutions. Research in both directions is being conducted at the University of Toronto.

DEPT. OF GEOLOGICAL SCIENCES,
UNIVERSITY OF TORONTO,
TORONTO, CANADA,
August 8, 1953.

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NOTES ON THE DUNITE AND THE GEOCHEMISTRY OF VERMICULITE AT THE DAY BOOK DUNITE DEPOSIT, YANCEY COUNTY, NORTH CAROLINA.[1]

J. LAURENCE KULP AND DONALD A. BROBST.

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ABSTRACT.

The Day Book dunite deposit of western North Carolina is a well-exposed ultramafic body representative of dunite deposits in the southern Blue Ridge Province. It was intruded after regional metamorphism had begun, but prior to pegmatite invasion. At the contact of the ultramafic body with the country rock, there is a zone ranging in thickness from several inches to a few feet, containing talc, enstatite, anthophyllite, and serpentine. Inside of this is a highly irregular zone of serpentine-talc that surrounds the granular olivine core. Chromite occurs in veins that strike approximately east. Vermiculite is found largely in north striking fractures. Pegmatites were intruded along joint planes in the dunite, and reaction of the dunite with the pegmatitic fluid progressively produced talc, asbestiform anthophyllite, and ferroan phlogopite. The formation of these minerals resulted in the desilication of the pegmatitic fluid. With subsequent weathering in the presence of excess magnesium ions, the phlogopite has been converted to vermiculite to a maximum depth of 40 feet.

INTRODUCTION.

THOUSANDS of ultramafic bodies ranging in length from a few feet to a mile or more have been noted in the Southern Appalachians. The ultramafic bodies have been intruded into the west limb (Blue Ridge Province) of the Appalachian geosyncline, which has its axis in the western Piedmont (9).[2] These bodies are described by Hunter and co-workers (7, 8, 11), with particular regard to their economic products, but detailed studies of the ultramafic bodies are rare.

[1] Publication authorized by the Director, U. S. Geological Survey.
[2] Numbers in parentheses refer to References at end of paper.

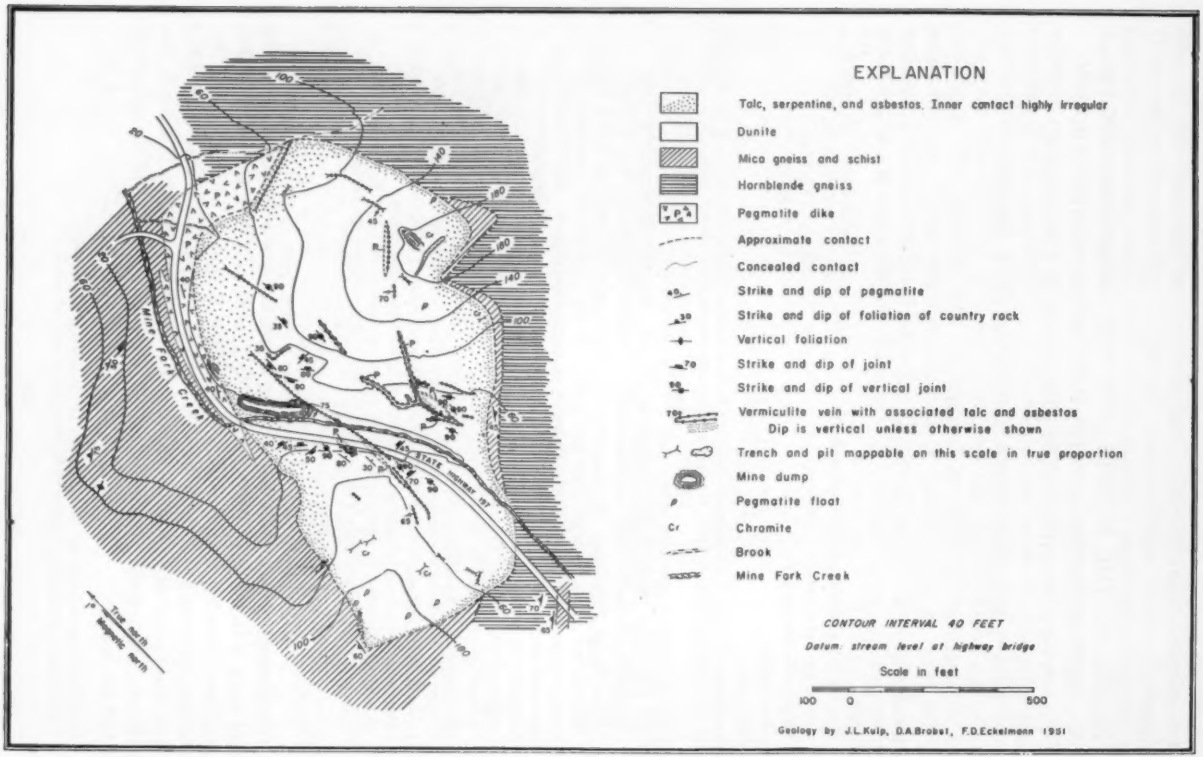

FIG. 1. Geologic map of Day Book dunite deposit.

The Day Book deposit is located on State Highway 197 and Mine Fork Creek about 3 miles north of Burnsville, Yancey County, N. C., just south of the junction of a secondary road to Day Book Post Office.

Development work of the American Vermiculite Co. has produced prospect pits, bulldozer roads, and clearings across the body. In addition a new highway has been cut through the center of the deposit. The intensive search for vermiculite at Day Book provides exposures that yield more data on the occurrence of this mineral than is available from most other ultramafic deposits in western North Carolina.

The authors wish to acknowledge the encouragement of R. A. Laurence, Regional Geologist, U. S. Geological Survey, in undertaking the study; the assistance of F. D. Eckelmann in mapping the deposit; and the suggestions of J. B. Hadley in preparing the manuscript.

The work upon which this report is based is part of a study of the North Carolina pegmatites, a cooperative program by the U. S. Geological Survey and the North Carolina Division of Mineral Resources, Department of Conservation and Development.

GEOLOGY.

The dunite deposits of western North Carolina are intruded into various types of gneisses and schists (7). In the Day Book area the country rock consists largely of mica gneiss interlayered with hornblende gneiss. Field relations suggest that the ultramafic intrusions occurred after the beginning of regional metamorphism but certainly before the invasion of pegmatites because the ultramafics are cut by the later pegmatites. Most geologists who have examined these alpine peridotites agree that the emplacement of the ultramafic bodies occurs during the early stages of regional metamorphism (14).

The map of the deposit (Fig. 1) shows that this dunite body is crosscutting in part and conformable in part. The body is bordered on the north by a large pegmatite, elsewhere by hornblende and mica gneisses. The divergent compositions of the two main types of gneiss appear to exert no influence on the dunite. Contrary to the suggestion of others (12) that the dunite or altered dunite (soapstone) bodies may be derived from the hornblende gneiss, it is clear from C. E. Hunter's study (7) of most of the significant ultramafic bodies in western North Carolina that the wall rock is just as likely to be mica gneiss as hornblende gneiss, and there is no evidence for the derivation of the ultramafics from the latter. This is consistent with the known and inferred origin of dunite in other metamorphic areas (6).

Border Alterations and Metamorphism.—The Day Book and other dunite deposits in this region show several important patterns of alteration. Most bodies display a talc-enstatite-anthophyllite-serpentine border zone that may range from a few inches to several feet in thickness. Inside of this border is a talc-serpentine alteration zone that merges irregularly with the essentially unaltered core of granular olivine (7). This is opposite from the relations noted by Hess (6) for dunites in Quebec and the Urals where the alteration is described as decreasing in intensity from the center outward. In the Day Book dunite the talc-serpentine alteration follows along joint planes to the

center of the body. In places the alteration pattern spreads out around the intersection of major fractures, but the broad pattern is clearly that of zonal alteration from the country-rock contact inward (Fig. 1).

These alteration zones at Day Book and other North Carolina dunite localities are generally unrelated to the country rocks or the later pegmatites. Furthermore, the serpentinization appears to be unrelated to weathering. This condition suggests that the serpentine and talc were formed during or shortly after dunite emplacement by the reaction of magnesian olivine with water and silica. The water and silica were probably derived in part from the surrounding rock. The total reaction evidently did not involve the transfer of large amounts of silica, but the transfer of some is indicated by the development of talc.

The present mineral constitution of an ultramafic body is dependent on its particular history. Consider the simplest theoretical case described by Bowen and Tuttle (2) of a mass of olivine and pyroxene crystals containing a trace of water as a lubricant intruded at 500° C. As the temperature of the mass cools below 500° C, serpentinization will take place as water reacts with the mass. Talc would also be formed if enough silica was supplied. This process would yield a peripherally serpentinized-steatized ultramafic deposit that would remain centrally unchanged. Repeated observation of this zonal alteration pattern in the dunites of western North Carolina suggests that this is the general process.

This simplified theory does not account for all the details. Field relations indicate that the ultramafic bodies were intruded prior to the thermal maximum of the regional metamorphism. Therefore, after emplacement and after development of the serpentine-talc zonal pattern, the bodies may have been heated to a higher temperature.

Difficulty arises in any attempt to ascertain the absolute temperatures involved. It appears that the only fixed point is 500° C, above which serpentine decomposes into olivine and talc, or talc and enstatite, depending on the composition. The temperature maximum attained in the regional metamorphism is much less subject to definition. Because Yoder (15) has demonstrated that the temperature of metamorphism cannot be defined by metamorphic grade, this common method of estimation is useless. A crude approximation of the temperature may be obtained from a consideration of the origin of the pegmatites. Presumably, these were formed from the early liquid fraction melted from the rocks some hundreds or thousands of feet below. The temperature range for such melting would probably be 500 to 600° C depending on the composition (14). The pegmatites, however, were intruded at a higher temperature than the surrounding rock as indicated by a fine-grained border zone. There is also evidence of abundant recrystallization in the gneiss and schist. It is probable, therefore, that the thermal maximum slightly exceeded 500° C.

How would the thermal maximum of regional metamorphism affect a dunite with a border of talc, enstatite, anthophyllite, and serpentine, an inner alteration zone of disseminated talc and serpentine, and an olivine core? If the temperature of the surrounding rock did not exceed 500° C, probably

nothing would happen to the dunite although the country rocks could be plastically deformed. If the temperature exceeded 500° C for a short time, serpentine in the border sheath would be altered to talc, enstatite, or olivine, but some might reform as the temperature again decreased. If the temperature of the entire body exceeded 500° C, all the serpentine would be decomposed, but some would re-form on cooling. It is unlikely that the temperature ever approached that of talc decomposition.

For those ultramafic rocks that were subjected to great shearing stress, considerable fluid may have passed through the entire mass. This fluid could have added silica and raised the temperature of the center of the body, resulting in the formation of impure soapstone. The most common minerals

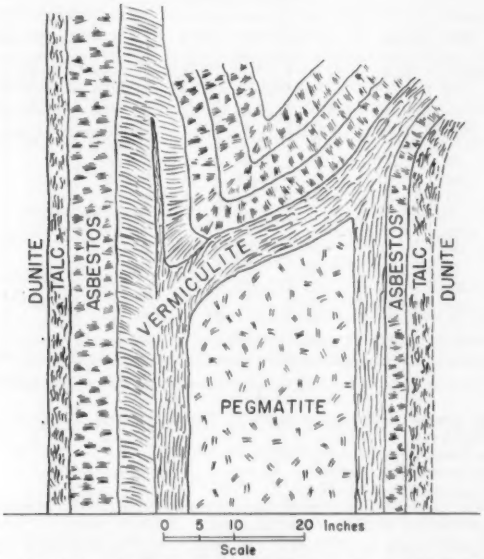

FIG. 2. Sketch of the alteration zones at the contact of the pegmatite and the dunite exposed along North Carolina highway No. 197 near the south border of Day Book deposit.

in the soapstone are talc, enstatite, and anthophyllite rather than serpentine. The latter, where present, appears to be later than the other minerals. Some serpentinization would be expected on cooling.

Chromite Occurrence.—Chromite in the ultramafic rocks of the Southern Appalachians is generally observed as disseminated crystals in an olivine matrix or as thin, discontinuous veins. The Day Book deposit contains many "showings" of chromite, both of the vein and disseminated types, although most are too small to mine. During 1917–1918, chromite was produced from the workings on the hill on the east side of Mine Fork Creek (Fig. 1).

Hunter (8) reports that this chromite occurs in a vein 15 inches wide and in many smaller veinlets.

An inspection of the map (Fig. 1) reveals that the chromite showings and workings strike roughly east and are independent of the trend of the country rocks, the border alteration, the pegmatites, and vermiculite. The parallelism of the veins suggests concentration in early formed planes of weakness. The common association of scattered talc might suggest that these chromite veins developed in planes along which some hydrothermal alteration occurred perhaps simultaneously with that which affected the border.

TABLE 1.

CHEMICAL ANALYSES.

	1*	2*	3*	4*	5	6	7	8	9
SiO_2	40.67	56.64	37.94	55.66	74.9	35.68	0.30	40.93	42.0
Al_2O_3	.75	1.43	11.44	25.05	14.9	14.53	21.30	1.32	17.1
Fe_2O_3	1.15	2.05	4.05	1.62		2.15	20.05	7.60	
FeO	6.56	4.86	.09	.45					2.3
MgO	48.77	29.68	25.84	2.00		24.65	14.48	48.77	25.4
CaO	.00	.21	.01	4.89	1.0	nil		0.29	—
Na_2O	.00	.01	.01	5.41	4.7	nil		0.13	—
K_2O	.03	.04	.05	.61	4.0	nil			7.6
H_2O	.08	.13	10.34	1.09					—
H_2O^+	1.38	3.71	9.67	3.09					4.4
TiO_2	.01	.02	.50	.08					
CO_2	.12	.01	.02	.01					
P_2O_5	.02	.02	.02	.09					
Cr_2O_3	.32	1.17	.00	—			44.20		
NiO	.31	.10	.10	—					
MnO	.12	.20	.07	.02					

* Samples 1–4 were taken on a line across the lower left side of the exposure illustrated in Figure 2.

1. *Day Book, dunite.* Analysis by Ruth H. Stokes, Denver Chemical Laboratory, U. S. Geological Survey, 3–14–52.
2. *Day Book, anthophyllite asbestos,* as above.
3. *Day Book, vermiculite,* as above.
4. *Day Book, pegmatite,* as above.
5. *Spruce Pine, pegmatite,* 500 tons of alaskite from Davis Quarry, Minpro, N. C., analysis by United Feldspar and Minerals Company.
6. *Day Book, vermiculite,* analysis by W. A. Reid, Chemist, Division of Mineral Resources, Dep't of Conservation and Development, Raleigh, N. C.
7. *Day Book, chromite,* analysis by W. A. Reid, as in 6.
8. *Day Book, dunite,* analysis by John Boyd, United Feldspar and Minerals Company, Minpro, N. C.
9. Hypothetical Day Book phlogopite calculated from vermiculite composition.

Pegmatite Intrusion.—As elsewhere in the Southern Appalachians, the pegmatites were intruded along joints and fractures in the dunite and along the contact between the dunite and the country rock. The reaction between such dissimilar rocks as pegmatite and dunite produced a specific sequence of minerals at their contact. The mineral sequence from the dunite to the pegmatite is talc, anthophyllite, and phlogopite. The phlogopite is weathered to vermiculite near the surface. Figure 2 is a sketch of one contact-alteration zone seen near the south border of the dunite body along State Highway No.

197. The great majority of pegmatites within the dunite body strike roughly north (Fig. 1) and presumably follow a primary joint pattern. The largest pegmatite body is along the arcuate contact between the country rocks and the dunite.

Significantly, all the larger ultramafic bodies examined in the Spruce Pine district and related areas are associated with later pegmatites. Thus, as will be seen below, practically all contain some vermiculite. The reason for this close association between pegmatite and dunite is probably structural. The contact of the dissimilar rock types and the jointed ultramafics provided excellent channels for mobile pegmatitic material.

GEOCHEMISTRY.

Table 1 shows analyses of some representative rocks and minerals associated with the Day Book dunite deposit. The first four samples were taken on a line across the lower left contact zone of the face illustrated in Figure 2. The dunite specimen taken 3–1/2 feet to the left of the dunite-talc contact was relatively unaltered. The vermiculite and anthophyllite asbestos

TABLE 2.

OPTICAL PROPERTIES OF DAY BOOK DUNITE MINERALS.

Olivine	2V = nearly 90°; good figure; β 1.670 ± .001; Composition $Mg_{90}Fe_{10}$* $Mg_{88}Fe_{12}$†
Anthophyllite	β 1.638 ± .001; γ = 1.65
Phlogopite	β 1.612 ± .002; 2V = 2–3° (This index suggests the ratio of Mg^{++} to Fe^{++} of 4:1)

* Winchell, Elements of mineralogy, 4th Ed., p. 500, John Wiley and Sons, N. Y. (1951).

† Larsen & Berman, Determination of non-opaque minerals: U. S. Geol. Survey Bull. 848, p. 239, 1934.

specimens were taken in the middle of their respective zones, which are virtually monomineralic. The pegmatite specimen was taken 6 inches to the right of the vermiculite-pegmatite contact. Table 2 gives the optical data for three of the minerals analyzed. The dunite is high in magnesium, and the pegmatite is low in iron content. This chromite sample is low in chromium, although Pratt and Lewis (13) give an analysis of chromite from the Day Book deposit containing 58.00% Cr_2O_3.

The reaction between the pegmatitic fluid and the olivine of the dunite produced an impure talc next to the unaltered olivine, anthophyllite asbestos next to the talc, and ferroan phlogopite adjacent to the desilicated pegmatite. A study of Tables 1 and 3 shows the successive chemical changes. A comparison of columns 4 and 5 (Table 1) shows that the pegmatite, after the reaction with dunite, is greatly reduced in silica and potassium. The iron and magnesium of the altered pegmatite were added from the dunite. The formation of a substituted phlogopite would yield a composition given in column 9 (Table 1), which was calculated from the vermiculite analysis. This shows the large increase in magnesia and corresponding decrease in silica and alumina compared to the adjacent altered pegmatite. The next stable phase toward the

dunite is anthophyllite, which shows an increase in silica, iron, and magnesia over the phlogopite and a sharp drop in alumina. An impure talc follows that is similar in composition to the anthophyllite with the exception that it contains less alumina. The tetrahedral alumina is lost in talc, but some octahedral alumina may remain as a minor constituent.

The sequence described above is the final result of the high temperature reaction. Subsequently, meteoric water at surface temperatures exchanges the Mg^{++} it carries for K^{+} present in the interlayer ions of phlogopite, thereby producing vermiculite (1, 4). Barshad (1) has demonstrated in the laboratory that this process goes on easily at the temperature, pressure, and water concentration of weathering conditions. Further evidence for the origin of the vermiculite by weathering processes is that the feldspar in the pegmatite adjacent to vermiculite is partially kaolinized and that the vermiculite gradually grades into essentially unweathered phlogopite at 10 to 40 feet below the surface. This limiting factor of depth has been found applicable in all other vermiculite deposits in this and neighboring counties.

TABLE 3.

IONIC CONTENTS OF MINERALS INVOLVED IN TRANSFORMATION OF DUNITE TO VERMICULITE AT DAY BOOK.

(Based on 12 oxygen positions)

	Ions per unit cell						
	Tetrahedral positions		Octahedral positions				
	Si	Al	Al	Mg	Fe^{++}	OH	K
Olivine	3	0	0	5.5	.5	0	0
Talc	4	0	.1	2.8	.1	2	0
Anthophyllite	3.5	.5	.1	2.8	.1	1	0
Phlogopite-Biotite	2.8	1.2	0.2	2.6	.1	2	.7
Vermiculite	2.8	1.2	0.2	2.95	.1	2^{+}	0

In some localities, the desilication of the pegmatite went far enough to produce a zone of alumina-rich hornblende and corundum between the phlogopite and pegmatite. Larsen (10) in 1928 summarized the data on a large number of corundum deposits and observed that these deposits were always found where pegmatite or albitite cross cut or contacted ultramafic rock. Further he noted that the sequence talc, anthophyllite, phlogopite-corundum-pegmatite was universal. Nevertheless, he did not accept the desilication thesis and suggested a hydrothermal origin of the corundum. In historical perspective, Larsen was entirely correct in two observations: 1. The chemical relations of the minerals surrounding these corundum bodies could not reasonably be accounted for by the reaction of a magma (i.e. low water, low volatile content, and high viscosity) with the ultramafic. 2. Where the pegmatite was thick enough, unaltered pegmatite could be found inside the albitite.

The data Larsen gave to support a hydrothermal origin can be more satisfactorily explained by a desilication theory if the modern concept (3) of the

nature of the pegmatitic fluid is applied. It seems clear that corundum is formed by desilication when one considers the following facts: 1. Albitites with corundum have not been observed outside of ultramafic bodies; 2. the areas around the ultramafic rocks inevitably show abundant normal pegmatites; 3. pegmatites that are sufficiently thick show albitite only along the contact with the ultramafic rock; and 4. pegmatites that cut the ultramafic-country rock contact are normal in mineral composition in the country rock but are albitite in the ultramafic. The answer to most of Larsen's arguments concerning the chemical relations lies in the nature of the pegmatitic fluid and the relative openness of the system. The observation that the width of the talc-anthophyllite-phlogopite zones tends to be independent of the size of the pegmatite is accounted for by similar temperature gradients and the rates of diffusion of ions. If reaction continues long enough, the total alteration cross section would be: unaltered dunite, talc plus olivine, talc, anthophyllite, phlogopite, hornblende with or without corundum, sodic plagioclase, granite pegmatite. Slight variations such as the insertion of actinolite and tremolite in place of anthophyllite will occur with variable concentrations of iron and calcium. These relationships have been described as occurring at other localities, e.g. Brinton's Quarry (10) and Buck Creek (5).

The reaction between the siliceous pegmatite and olivine at Day Book is idealized below. These formulas were developed from the analytical data on the different minerals, with the exception of the talc formula, which is hypothetical. All formulas are based on 12 oxygen or OH ion positions in the lattice.

$$Mg_{5.48}Fe_{.52}Si_3O_{12}$$
Day Book Olivine

$$\downarrow$$

$$Mg_{2.8}Fe_{.1}Al_{.1}Si_4O_{10}(OH)_2$$
Talc

$$\downarrow$$

$$Mg_{2.8}Fe_{.1}Al_{.1}(Si_{3.5}Al_{.5})O_{10}(OH)$$
Anthophyllite

$$\downarrow$$

$$K_{.66}\,(Mg_{2.59}{}^{+}Al_{.20}{}^{+}Fe_{.13})\,(Si_{2.84}{}^{+}Al_{1.16})O_{10}(OH)_2$$
Day Book Phlogopite

$$+$$

$$Mg^{++}\,\text{(weathering)}$$

$$\downarrow$$

$$Mg_{.33}(Mg_{2.59}{}^{+}Al_{0.20}{}^{+}Fe_{0.13})\,(Si_{2.84}{}^{+}Al_{1.16})O_{10}(OH)_2 \times H_2O$$
Day Book Vermiculite

Early workers generally considered vermiculite a hydrothermal product, but this is certainly not the case in the Southern Appalachians. The absence of significant quantities of vermiculite in the New England States, where similar ultramafics are cut by pegmatites, is related to the glacial scour of pre-Pleistocene weathered rock.

CONCLUSIONS.

1. Dunite emplacement occurs at fairly low temperatures in the early phases of regional metamorphism.

2. The pegmatites invaded the dunite along contacts and joints later in the metamorphic cycle.

3. The reaction of the ultramafic rock with the pegmatitic fluid produces successively talc, anthrophyllite, and phlogopite (and rarely hornblende and corundum).

4. Phlogopite, on weathering in this high-magnesium environment, alters to vermiculite.

5. The reserves of vermiculite in these bodies are limited to the depth of the zone of weathering. Below that depth, vermiculite grades into unaltered phlogopite.

6. The reserves of vermiculite at Day Book are probably located along the north-trending fractures, along the contact of the pegmatite on the north side of the deposit, and at the intersection of major fracture systems (see the central-southeast workings in Fig. 1).

7. These geochemical and geological principles should be widely applicable to other similar deposits.

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August 17, 1953.

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SCIENTIFIC COMMUNICATIONS

DISSEMINATED SCHEELITE IN THE LITTLE COTTONWOOD STOCK, UTAH.

MAX P. ERICKSON AND BYRON J. SHARP.

The Little Cottonwood "Granite," located about 25 miles east of the Bingham copper pit, has been rather well known since it was described in a report of the 40th parallel survey (3). Several works refer to the stock in its association to the similar, but smaller, intrusives of the Alta and Park City mining districts, which lie respectively to the east. Best known of these works is that by Calkins and Butler (2).[1] Calkins refers to the rock as the Little Cottonwood quartz monzonite, but he found a separate facies in the eastern part of the stock. This article presents evidence for a separate intrusion, which will be designated as the White Pine intrusive phase, and announces the occurrence of widespread scheelite occuring throughout the northeastern part of the Little Cottonwood stock. Geological studies in the area are in progress and a detailed account of the geology will be published when completed.

LITTLE COTTONWOOD QUARTZ MONZONITE AND WHITE PINE PHASE.

The Little Cottonwood quartz monzonite occupies an area of about 25 square miles. The rock, as described in detail by Calkins, is granitic and prophyritic in texture. The granitic groundmass is granodioritic in composition but large potash feldspar phenocrysts are sufficiently abundant to make the overall composition quartz monzonite.

The White Pine phase, classified also as a quartz monzonite, is a roughly elliptical outcrop in plan elongated in an east-west direction. It is about 2 miles long and 1½ miles wide, and is completely surrounded by Little Cottonwood quartz monzonite. It occurs near the eastern edge of the quartz monzonite, and is exposed mainly in the White Pine Fork of Little Cottonwood canyon and also in the east side of Red Pine Fork.

The Little Cottonwood quartz monzonite differs from the White Pine phase in many respects. The dark mineral content is 6 to 10 percent in contrast to 3 and 6 percent for the White Pine phase. Both biotite and hornblende are present, whereas only biotite is present in the White Pine phase. Sphene and dark inclusions are characteristic of the Little Cottonwood quartz monzonite and are apparently absent from the White Pine phase. The late orthoclase phenocrysts stand out in relief on weathered surfaces of the normal

[1] Numbers in parentheses refer to References at end of paper.

quartz monzonite, but appear as square outlines which do not weather out in relief in the White Pine phase exposures.

MINERALIZATION.

The known introduced or secondary minerals are quartz, pyrite molybdenite, scheelite, muscovite, calcite, galena, sphalerite, and fluorite.

The mineralization has a zonal arrangement that is essentially concentric with respect to the White Pine phase and may be described in terms of three rather distinctive zones consisting of a central breccia pipe zone surrounded successively by a stockwork zone, and a fringe zone of mild mineralization consisting of quartz, pyrite, and muscovite. This mineralization seems to be similar to that found at the Climax, Colorado, molybdenum deposit described by Butler and Vanderwilt (1).

Breccia Pipe.—The breccia pipe constitutes the innermost zone and is located within and near the south edge of the White Pine phase. It is essentially circular in outline and is about 1,000 feet in diameter. The rock in the pipe is intensely broken and veined with quartz, to the extent that the rock is difficult to determine. The pipe as a whole is reddish in color and massive in appearance. Minerals associated with the quartz are pyrite, molybdenite, calcite, fluorite, and very minor amounts of scheelite.

Stockwork Zone.—The stockwork zone appears to surround the breccia pipe. It is an elongated zone with a length of about 1½ miles and a width of about ½ mile with closely spaced quartz veins. The long dimension of the zone is east-west and it cuts almost through the center of the White Pine quartz monzonite. Minerals found associated with the quartz are pyrite and molybdenite but they occur in lower concentrations here than in the breccia pipe. The host quartz monzonite is discolored to brown but is generally determinable and can be distinguished from the Little Cottonwood quartz monzonite by the features listed above.

Fringe Zone of Mineralization.—Beyond the stockwork, mineralization is confined largely to joints. Minerals present are pyrite, quartz, muscovite, and scheelite. The quartz, pyrite and scheelite appear to diminish in quantity away from the stockwork area, and in the inner zones are probably connected with the more localized mineralization.

A few thick quartz veins are present here, cutting the rocks of the fringe zone. Some of these contain galena, sphalerite and pyrite but others contain some molybdenite and pyrite.

The muscovite occurring on the joint surfaces is spread throughout the zone and seems to be a late magmatic effect rather than a localized, secondary mineralization feature. Beyond the fringe zone the quartz monzonite has minor amounts of pyrite on the joint surfaces and within the fresh rock.

OCCURRENCE OF SCHEELITE.

The scheelite in the joint systems of the fringe zone is disseminated and appears to constitute a type of deposit that has not been previously recognized.

Scheelite is present as scattered, small (0.5 to 0.01) mm in diameter) crystals along with introduced pyrite and quartz in the joints. The associated muscovite may have been introduced but more likely it is the result of widespread late magmatic readjustments.

Concentration of scheelite in the joints is quite marked. Scheelite appears to constitute at least ½ to 1 percent of the material in the joints; however, the amount present in any sizable block of rock is obviously much lower because the scheelite is limited to the fractures and is not disseminated through the rock. One sample taken at random from the weathered outcrop without the use of an ultraviolet light contained .02 percent of WO_3. It is probably indicative of the order of magnitude of the total tungsten content of the rock.

The scheelite occurs on joints of several different attitudes, at any one locality, however, it may be more concentrated on one joint set. The scheelite distribution seems to fit the zonal arrangement described above for the other introduced minerals. It is apparently confined to a zone several square miles in extent surrounding the stockwork and seems to be quite uniformly distributed. It is found in both the Little Cottonwood and White Pine phases of the quartz monzonite and observations show a vertical range of 3,000 feet with no apparent variation in concentration.

Economic Possibilities.—The distribution of scheelite in the outer mineralized zone indicates a single, localized, large, very low-grade tungsten deposit of a new type. The total amount of tungsten in the deposit may be very large and it exists in a recoverable form. The deposit may possibly have economic significance at the present time but, more likely, will be more significant in the future.

Factors that could make the deposit of immediate significance are: (1) Sudden need for tungsten in large quantities due to new industrial advances. (2) Government interest in subsidizing development work in order to have a readily available domestic supply. (3) Curtailing of foreign supplies of tungsten. (4) Presence of other by-product ores which would contribute to the value of the deposit.

The mineralization responsible for the stockwork and breccia pipe zones might have resulted in more concentrated ore bodies of a localized nature. Known mineralization in these zones suggests that a search should be continued for elements commonly associated with high temperature deposition such as molybdenum, tungsten, gold, and tin.

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REVIEWS

Conversation with the Earth. By HANS CLOOS. Translated by E. B. GARSIDE. Pp. 413; pls. 52; figs. 26; tbl. 1. Alfred A. Knopf, New York, 1953. Price, $5.75.

This charming autobiography by Hans Cloos deals with his travels throughout various parts of the world. It is a story rather than geology. Incidentally, the amount of geology is relatively small, but the experiences of the geologist in travelling, and what he saw, are delightfully recorded here. The autobiography starts off with a prologue, Part I, dealing with Africa, in which he takes up his various travels there to the diamonds in the desert sands and the deepest landscape on earth, meaning the Witwatersrand gold mines. In Part II he takes up the Indies, touching briefly on volcanoes and mountains. Then he jumps to the northland where he saw the basic complex and the older deep-seated rocks of the northern Scandanavian peninsula, and likewise those of the North American continent. He records his journeys in Utah, and California, and Arizona. His Part V deals with an historical trip through Germany—the familiar places that we all like to read about. Part VI is his so-called last journey, which deals with Africa, the Red Sea and his journeys in those particular regions. Many excellent photographs illustrate some of the things that he saw, but more particularly, the reader is impressed by the inimitable drawings for which Hans Cloos is so noted, and they are rather profuse throughout the book.

The book is dramatically written and describes the enormous changes that are constantly going on in familiar landscapes. The whole material is written in an absolutely layman's style and anyone who could sit down and enjoy *The Sea Around Us* can also enjoy this book, which is very similar to it. This is a book that not only geologists would wish to read, but more particularly the layman who is interested in geology, or interested in earth features, without even giving it the name, geology. Rather humdrum observations are turned into exciting and dramatic events by the author in his excellent choice of language. We highly recommend it.

Anleitung zu optischen Untersuchungen mit dem Polarisationsmikroskop. By MAX BEREK. Edited by C. H. CLAUSSEN, A. DRIESEN and S. RÖSCH. Pp. xiii, 366; figs. 285; tbls. 21. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 1953. Price, DM 29.—.

It is indeed unfortunate that this comprehensive text is not more readily available: the language barrier will probably deter most American students from using it. Nevertheless, it is a highly readable book and is recommended especially for teachers of petrographic techniques and users of polarizing microscopes.

The title is somewhat misleading since it gives no indication of the scope or substance of the subject matter. It covers equally completely such seemingly diverse material as wave optics, polarized light, the polarizing microscope including its construction and application, crystal structure, stereographic projections, crystal morphology, and the methods of determining optical properties of opaque and non-opaque minerals. The material is so arranged that it is suitable as a text on the elementary or intermediate levels; but advanced students will derive much

satisfaction from using it: it contains, for example, comprehensive treatments of microphotography and the universal stage.

Historical interest in optical mineralogy is stimulated by reference of all concepts and methods to their original description. The many illustrations and plates are uniformly excellent; the line drawings are lucidly annotated and of a high caliber. A novel nomenclature may appeal to the reader: namely, the words digyre, trigyre, tetragyre, and hexagyre denote two-, three-, four-, and six-fold axes of symmetry. These simple descriptive terms are commendable compared to the cumbersome English equivalents. The crystal-class notation used is that of Rinne the established international symbols are unfortunately not mentioned. A center of symmetry is symbolized SZ (*Symmetriezentrum*); axis of symmetry, SA (*Symmetrieaxe*); plane of symmetry, SE (*Symmetrieebene*); and reflection axis of symmetry, SSA (*Spiegelungssymetrieaxe*). Crystal forms are derived from five basic ones by use of these elements.

The usefulness of this book is enhanced by the virtual absence of errors and by a descriptive final chapter named "Übungsbeispiele für optische Untersuchungen" keyed to a set of oriented sections by a well-known German firm. The first edition of this work has long been out of print, therefore this revision is especially welcome. Regretfully, the author was not destined to witness its publication.

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February 3, 1954.

A Field Guide to Rocks and Minerals. By FREDERICK H. POUGH. Pp. 333; figs. 34; pls. 44. Houghton Mifflin Company, New York, 1953. Price, $3.75.

Dr. Pough in this book has prepared a pocket handbook which is intended to satisfy particularly the interest of the amateur, but it is also carefully prepared enough that it can serve as an excellent guide for the beginner in mineralogy. It covers all of the common minerals and is illustrated by 254 photographs, of which 72 are in full color, rather beautifully done. The book compresses into a small space an enormous amount of information about minerals that should fill all the interests of the amateur and supply much interest for the student in geology. Chapter 1 deals with one's mineral collection. Chapter 2 deals with rocks and minerals and where to find them, with a summation of the various kinds of rocks. Chapter 3 gives the physical properties of minerals with their distinguishing characteristics. Chapter 4 takes up crystal classifications, which is a bit strong for the ordinary amateur. Chapter 5 takes up the chemical classification of minerals, according to elements, sulfides, oxides, etc. In Chapter 6 the author deals with tests, techniques, and, as he calls it, tips. Then Part II takes up the various minerals in succession. A valuable glossary occurs at the end and a good bibliography. In the last part, emphasis is placed on the immediate identification in the field, which is a very useful type of thing for the collector when he is out in the field itself.

This is a handy little book which certainly should be welcomed by the mineral collector.

Rutley's Elements of Mineralogy, 25th ed. By H. H. READ. Pp. 525; figs. 137. Interscience Publishers, New York, no date. Price, $2.50.

On the jacket the title is followed by "A reprint of the 24th edition with a new chapter on the Atomic Structure of Minerals." but the same new chapter was part

of the 24th edition. Some details in this chapter may be questionable, as on pp. 134–5 where we read that the residual bond is important "in the realm of organic substances," leaving the impression that it is unimportant in minerals; but later we find that talc has such bonds (p. 144). Again, discussing the structure of olivine (p. 140), "* * * every tetrahedral group is linked to two divalent ions * * *." In fact, since every Mg is coordinated with 6 oxygens, there must be three Mg about each O, and each SiO_4 group must therefore be linked to four or more Mg.

The arrangement of minerals by metals of which they are ores inevitably produces odd results among the silicates. Beryl, spodumene, and zircon are described with Be, Li, and Zr minerals, respectively, but lepidolite is with the silicates. Silicates are subdivided into "rock-forming," and "less abundant but important" silicate families, placed in separate series ordered according to structural types.

Although Professor Read's economic arrangement of minerals may be criticized, it is an eminently practical one for teaching, and one that can be recommended in spite of differences of opinion as to the best arrangement of minerals.

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February 5, 1954.

Tin, 1951–1953. Review of World Tin Industry. Pp. 100; figs. 7. International Tin Study Group, Carel van Bylandtlaan, The Hague, Holland, 1953. Price, $1.00.

This new Review covers the two years to June 1953, and, therefore, deals with a period in which the tin industry was subject to very important changes. The present book deals with the international position in tin, the world production position, world consumption, smelter position, trade in tin, world stocks, prices, tin-plate position, the use of tin and tinplate. The appendices take up prices in London, New York and Singapore, prices of concentrates, consumption of tin metal and also by areas, world stocks of tin, imports of tinplate and export of tin to Eastern Europe. The volume also gives considerable space to the position of the United States with respect to its tin smelter and its importation of concentrates as well as its production of metal. The book is well supported by statistics for the areas except the Soviet, and numerous charts display this rather concisely.

A supplement, 1953, to the statistical yearbook covers tin, tinplate and canning and takes up the position with all the same countries, again with the exception of the Soviet.

Manual of the Polarizing Microscope. By A. F. HALLIMOND. Pp. 204; figs. 92. Cooke, Troughton & Simms, Ltd., York, England, 1953. Price, 15/–.

This little book is a curious mixture of technical information and advertisement for the Cooke microscope. It is larger, by 97 pages, than the first edition which appeared in 1948. Four new chapters are entitled "Measurement of Rotation and Path-difference in Reflected Light" (9 pp.), "The Visual Microphotometer" (6 pp.), "The Universal Stage" (28 pp.), and "Mounting and Polishing Specimens" (13 pp.). There are two new appendices: "Adjustment of Universal Stage" (5 pp.) and "Table of Sin, Sin^2 and Sin^4" (3 pp.) in addition to 43 new illustrations and many recent references in the bibliography.

The book is designed as a guide for the use of the Cooke microscopes. The entire second chapter is devoted to a description of its design and accessories

(11 pp.). Much interesting information of historical development is included in the beginnings of most of the chapters.

Two innovations for the American reader which warrant mention and encouragement involve semantics. The author advocates and adheres to the usage of the word "polars" to designate any unit for producing or analyzing plane-polarized light. This is appropriate since the Cooke microscope, as well as the inexpensive domestic "student" microscopes, contains polaroid in place of the conventional calcite Nicol prisms. Another admirable suggestion is the replacement of "directions image" for the older "interference figure."

There are occasional errors and inconsistencies in the text; most of these may be ascribed to careless editing. One inconsistency which is unfortunate is that o and e designate uniaxial vibration directions; α, β, and γ, the principal refractive indices of biaxial minerals; and X, Y, Z, the "optical symmetry axes." The reproduction of illustrations is somewhat erratic: many of the plates are excellent, but some of the text figures are indistinct so that their salient features are obscure.

This manual is an adequate treatise for the intermediate student; however, the beginner will find it difficult inasmuch as it makes generous assumptions that the reader is familiar with the groundwork of petrographic methods. A comprehensive chapter on polished sections is included for the mineralographer.

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Morphological Analysis of Land Forms. By WALTHER PENCK. Translated by HELLA CZECH and KATHERINE CUMMING BOSWELL. Pp. 429; pls. 12; figs. 21. St. Martin's Press, New York, 1953. Price, $8.00.

Dr. Penck's book was published in 1924 but as it was not generally available to Americans it was little known to many. This quite good translation now makes it available to all English readers.

It deals with the generally familiar subjects of physical geology such as The Earth's Crust, Reduction of Rock Material, Mass Movement, Development of Slopes and Land Forms. The book was incomplete when he died in 1923. The translators have inserted 51 pages of notes on the original chapters. Much of the material is naturally out of date as Albrecht Penck published the original as it stood without any editing and the translators have followed this rather closely.

A German-English and English-German glossary is at the end of the book.

It is interesting reading for anyone interested in Dr. Penck's early ideas.

BOOKS RECEIVED

FRANK G. LESURE

U. S. Geological Survey—Washington, 1953

Bull. 1000-A. Geochemical Prospecting Abstracts Through June 1952. JOHN W. HARBAUGH. Pp. 50. Price, 20 cts. *Abstracts of world literature on geochemical prospecting methods.*

Geology of the Galice Quadrangle, Oregon. F. G. WELLS AND G. W. WALKER. *Includes map, scale 1:62,500, and brief description of stratigraphy and structure.*

TEI-330. Search for and Geology of Radioactive Deposits, Semiannual Progress Report, December 1, 1952 to May 31, 1953. Pp. 302; figs. 37; tbls. 11. *Progress reports on: the search for and geology of uranium deposits in sandstones, veins and igneous rocks, carbonaceous rocks, and phosphate; the search for and geology of thorium and monzonite deposits; regional reconnaissance for uranium and thorium in United States and Alaska; chemical, geochemical, petrographic, mineralogic and geophysical service and research methods.*

Circ. 305. Stratigraphic Sections of the Phosphoria Formation in Idaho, 1949, Part 2. D. F. DAVIDSON, R. A. SMART, H. W. PIERCE, AND J. D. WEISER. Pp. 28; figs. 2.

Circ. 311. A Fluorimeter for Solutions. MARY H. FLETCHER AND E. RAY WARNER. Pp. 9; figs. 8. *Description and complete drawings for construction of fluorimeter.*

Circ. 312. Yellow Canary Uranium Deposits, Daggett County, Utah. V. R. WILMARTH. Pp. 8.

Circ. 313. Reconnaissance for Uranium-Bearing Carbonaceous Rocks in California and Adjacent Parts of Oregon and Nevada. GEORGE W. MOORE AND JAMES G. STEPHENS. Pp. 8; figs. 2; tbls. 6.

Circ. 319. Reconnaissance for Uranium in the Lost River Area Seward Peninsula, Alaska, 1951. MAX G. WHITE AND WALTER S. WEST. Pp. 4; fig. 1; tbl. 1.

Circ. 320. Uranium Occurrences in the Golden Gate Canyon and Ralston Creek Areas, Jefferson County, Colorado. J. W. ADAMS, A. J. GUDE 3D, AND E. P. BERONI. Pp. 16; figs. 9; tbl. 1.

U. S. Atomic Energy Commission—Oak Ridge, Tennessee, 1953.

RMO-982 (rev.). Uranium Deposits in Southwestern Colorado Plateau. GEORGE W. BAIN. Pp. 59; figs. 19; tbl. 1.

RME-3067. Sedimentary Properties of Salt Wash Sandstones as Related to Primary Structures. WILLIAM LEE STOKES AND WALTER SADLICK. Pp. 26; figs. 6; tbl. 1.

RME-4011. Investigation of the "C" Group Area, San Juan County, Utah. PAUL C. DEVERGIE AND WILLIAM A. CARLSON. Pp. 13; figs. 4.

RME-4018. Results of Exploration at the Copper King Mine, Larimer County, Colorado. RAYMOND C. DERZAY AND KENNETH E. BAKER. Pp. 16; figs. 3.

RME-4020. Preliminary Report on Relation of Structure to Uranium Mineralization in the Todilto Limestone, Grants District, New Mexico. PHILIP C. ELLSWORTH AND ARTHUR MIRSKY. Pp. 15; figs. 8.

RME-4022. The Uranium Deposits of Big Indian Wash, San Juan County, Utah. GEORGE P. DIX, JR. Pp. 15; figs. 6.

RME-4037. Preliminary Reconnaissance of the Dripping Spring Quartzite Formation in Gila and Pinal Counties, Arizona. W. E. MEAD AND R. L. WELLS. Pp. 9; pl. 1.

RME-4039. Drilling in the Happy Jack Mine Area, White Canyon, San Juan County, Utah. LEO J. MILLER. Pp. 14; figs. 7.

Sedimentation in Cold Springs Reservoir, Umatilla County, Oregon. Pp. 26; figs. 13; tbls. 5. U. S. Department of Agriculture, Soil Conservation Service, Pacific Region, 1953.

California Division of Mines—San Francisco, 1953.

Bull. 164. Geology of Eel River Valley Area, Humboldt County, California. BURDETTE A. OGLE. Pp. 128; pls. 6; figs. 14. *Contains geologic map, 1:62,500.*

Bull. 168. Geology of the Breckenridge Mountain Quadrangle. T. W. DIBBLEE, JR. AND CHARLES W. CHESTERMAN. Pp. 56; pls. 3; figs. 32. *Contains geologic map, 1:62,500.*

Special Rept. 33. Geology of the Griffith Park Area, Los Angeles County, California. GEORGE J. NEUERBURG. Pp. 29; pl. 1; figs. 15. Price, 50 cts.

Special Rept. 35. Tungsten Deposits of Madera, Fresno and Tulare Counties, California. KONRAD B. KRAUSKOPF. Pp. 83; pls. 4; figs. 52. Price, $1.25. *Includes descriptions of five important mines and maps and sections of others.*

California Journal of Mines and Geology, Vol. 49, No. 4. Mines and Mineral Resources of Mendocino County, California. J. C. O'BRIEN. Pp. 341–418; pl. 1; figs. 4. **De Argento Vivo, Historic Documents on Quicksilver and Its Recovery in California Prior to 1860.** ELISABETH L. EGENHOFF. Pp. 144. *Chronicle of quicksilver and early mining in California prior to 1860; contains extracts from early writings on quicksilver back to 300 B.C.; descriptions of early California mines by visitors.*

Illinois Mineral Industry in 1951 and 1952. WALTER H. VOSKUIL. Pp. 52; figs. 17; tbls. 39. Illinois Geological Survey, Rept. of Inv. 168, Urabana, 1953. *Statistics on production and development of coal, coke, petroleum and nonmetallic mineral industries.*

Petroleum exploration maps; well location maps showing total depth of wells: nos. 3a, Warrick County; 12a (rev.), Martin County; 13a, Greene County; 14a, Clay County; 15a, Parke County; 16a, Vermillion County; 17a, Fountain County; 18a, Owen County; 19a, Putnam County; 20a, Montgomery County; 21a, Dubois County; 22a (rev.), Jackson County; 24a (rev.), Monroe County; 25a (rev.), Lawrence County; 27a (rev.), Orange County; 28a (rev.), Crawford County; 29a (rev.), Washington County; 30a (rev.), Harrison County; 31a (rev.), Brown County; 38a, Warren County. Scale 1 inch to 1 mile. Geological Survey of Indiana, Bloomington, 1953.

Ohio Geological Survey—Columbus, 1953.

Inf. Circ. 12. Our Natural Resources: Their Continuing Discovery and Human Progress. MORRIS M. LEIGHTON. Pp. 16; figs. 2.

Inf. Circ. 2. Water Resources of Scioto County, Ohio. ALFRED C. WALKER AND JAMES J. SCHMIDT. Pp. 17; pls. 8; tbls. 3.

Virginia Mineral Localities. RICHARD V. DIETRICH. Pp. 57. Bull. of Virginia Polytechnic Institute, Engineering Experiment Station Series No. 88, Blacksburg, 1953. Price, 50 cts. *Lists minerals and localities in which they occur.*

Functions and Responsibilities of a Company Coal Mine Inspector. J. A. BOYLE. Pp. 3. U. S. Steel Corp. Tech. Paper No. 92, New York, 1953.

Clay Minerals. TOSHIO SUDO. Pp. 240; figs. 79. Iwanami Series, No. 178, Iwanami-shoten, Tokyo, 1953. *Small, compact book in Japanese; includes discussion of study methods, mechanical separation, megascopic, microscopic, x-ray, electron microscope, and differential thermal analysis; discussion of crystal structure and chemistry of clay minerals.*

An Introduction to the Theory of Seismology. K. E. BULLEN. Pp. 259; figs. 43. Cambridge University Press, New York, 1954. Price, $6.50. *Discusses fundamentals of elasticity, the theory of wave-motion, the theories of waves of dilation and distortion, principles of seismographs, construction of travel time-tables, inferences on constitution of earth's crust and interior based on earthquake records, and practical considerations of earthquake studies.*

Canada Department of Mines—Ottawa, 1953.

National Advisory Committee on Research in the Geological Sciences, Third Annual Rept. Pp. 124.

Preliminary Report on the Geology of Parts of Long and Spragge Townships, Blind River Uranium Area, District of Algoma. E. M. ABRAHAM. Pp. 10; pl. 1. *Uranium deposits in quartz-pebble conglomerate.*

Quebec Department of Mines—Quebec, 1953.

Geol. Rept. 53. Albanel Area, Mistassini Territory. JAMES M. NEILSON. Pp. 35; pls. 5. *Brief description of stratigraphy and structure of area.*

Geol. Rept. 57. Allard River Area, Abitibi-East County. RENÉ BÉLAND. Pp. 26; pls. 9; fig. 1. *General geology and structure of area.*

Geol. Rept. Waswanipi Lake Area. (West half.) JACQUES CLAVEAU. Pp. 31; pls. 9. *General geology and structure of area.*

Geol. Rept. 59. Waswanipi Lake Area. (East half.) DONALD A. W. BLAKE. Pp. 23; pls. 9; fig. 1. *General geology of area.*

Report of the Government Chemical Laboratories, 1950. Pp. 57. Western Australia Mines Dept., Perth, 1953.

Relatório de 1951. Pp. 269; figs. 22. Conselho Nacional do Petrólio, Rio de Janeiro, 1952. *Annual report; includes statistics on production of oil and gas, reserves, refining and exploration.*

Report on the Geological Survey Department for the Year 1952. Pp. 101; figs. 7. Geol. Survey of British Guiana, Georgetown, 1953. Price, $1.00. *Contains seven short papers on gold, diamonds, columbite and bauxite deposits.*

Geotektonische Forschungen. Heft 9/10. Zur germanotypen Tektonik IV (Osningtektonik I). Pp. 115. E. Schweizerbart'sche Verlag., Stuttgart, 1953. *First issue since 1945 of journal concerned with tectonics. Contains seven papers on the tectonics of Saxony.*

Zentralblatt für Geologie und Paläontologie—E. Schweizerbart'sche Verlag., Stuttgart, 1952–53.

Teil II. Historische Geologie und Paläontologie. Heft 3, Paläontologie. Pp. I–CLI, 615–778. *Contains listing of recent literature on historic geology and paleontology; reviews of some longer articles; index for 1952.*

Teil I. Allgemeine und Angewandte Geologie einschl. Lagerstättengeologie, Regionale Geologie. Heft I. Pp. 164. *Listing and reviews of books and papers on general geology, applied geology and regional geology.*

Geologie—Akademie Verlag, Berlin, 1952–53.

Jahr. 1, Nr. 6. Pp. 413–474. *Includes a paper on the System SiO_2–H_2O; and study of colloidal structures in zincblende and wurtzite.*

Jahr. 2, Nrs. 1–3. Pp. 1–228.

Beiheft Nr. 2. Pp. 99; figs. 44. *The Mecklenburg high bogs; description and stratigraphy of the Mecklenburg bogs and their relationships to other bogs in Europe.*

Beiheft Nr. 3. Pp. 27; figs. 18. *Genetic interpretation of kaolin and clay deposits of Saxony based on geologic and petrologic studies.*

Beiheft Nr. 4. Pp. 37; figs. 6. *The magnetite concentrations of the Harz gabbro and their tectonic importance.*

Beiheft Nr. 5/6. Pp. 320. *The geologic literature of Saxony, 1921–1950.*

The Geology and Gem-Stones of the Mogok Stone Tract, Burma. L. A. N. IYER. Pp. 100; pls. 8. Memoirs of the Geological Survey of India, Vol. 82, Calcutta, 1953. Price, Rs 4/12.

Boletin de Estadística Peruana. Pp. 233. Ministerio de Hacienda y Comercio, Lima, 1952.

Memórias e Notícias—Coimbra, Portugal, 1952–53.

No. 32. Pp. 64. *Includes papers on granites in Noqui and Nova Lisboa in Angola and Guarda; diamond deposits of Lunda, Angola; qualitative spectrographic analyses of 34 Portugese wolframites; and occurrence of uranium-bearing minerals in N. Portugal.*

No. 33. Pp. 67. *Papers on terrestrial magnetism; genesis of the principal iron deposits of Portugal, occurrences of pigeonite dolerite and basalt in Angola and studies on Pleistocene and Recent sediments in Portugal.*

No. 34. Pp. 66. *Contains papers on: fossil fauna of Inhaminga, studies of Pliocene-Pleistocene sediments of Portugal, granites of Urgeirica and notes on the climate of Coimbra.*

SCIENTIFIC NOTES AND NEWS

Canada's oldest living professional engineer, J. B. TYRRELL, 95, of Toronto, explorer and geologist, received the coveted Engineer's Medal at the annual meeting of the Association of Professional Engineers of Ontario in February. The citation accompanying the award acclaimed him for his outstanding achievements in the field of mining engineering and his contribution to the Canadian economy.

THE NATIONAL SCIENCE FOUNDATION has announced 100 grants totaling about $1,045,000 for research in the biological and the physical sciences, and to support studies and conferences on science, scientific information exchange, compilation of scientific personnel information, education in the sciences and travel of American scientists to international scientific meetings.

H. W. STRALEY, III, geologist and geophysicist, Princeton, W. Virginia, is currently engaged in electrical and magnetic investigations of iron deposits in northern Georgia.

D. P. BARNARD of Chicago, research coordinator for the Standard Oil Company (Indiana), was sworn in as Deputy Assistant Secretary of Defense on February 1. In this position he will be deputy to Donald A. Quarles, Assistant Secretary of Defense (Research and Development).

THE SOUTHWEST RESEARCH INSTITUTE has announced the addition of ten scientists and technicians to its staff during recent months. The new personnel includes: ORIN M. ANDERSON, S. J. BACKEY, RAYMOND CAPPEL, GEORGE COYLE, RAYMOND A. GARREN, VICTOR C. KOBOLD, HOWARD A. LANGAN, WALTER K. MORRIS, JAMES G. PAULY, and S. H. SIMPSON, JR.

PHILIP D. WILSON, mining engineer and geologist, has announced an arrangement on January first with Lehman Brothers and the Lehman Corporation whereby a portion of his time will be available for consultation and for the examination and evaluation of mines and of mining securities for other clients.

THE MINING AND METALLURGICAL SOCIETY OF AMERICA has announced the election of the following officers for the current year: ALAN M. BATEMAN, President; PHILIP D. WILSON, Vice-President; DONALD M. LIDDELL, Secretary-Treasurer; and for Councilors, ROBERT P. KOENIG, HOWLAND BANCROFT, EVAN JUST, EDWARD W. ENGLEMANN and SAMUEL H. WILLISTON.

TOM LYON, until recently with DMPA, has joined Southwestern Engineering Co., of Los Angeles, in the capacity of consulting engineer.

GLEN S. WYMAN has been appointed general superintendent at Chuquicamata. L. E. Fish succeeds him as superintendent at the Chile Exploration Co. operations.

ALAN GIBSON, senior geologist, Mount Isa Mines, has joined the South Australian Department of Mines.

FRANK L. STILLWELL has retired from the CSIRO Mineragraphic Section, Melbourne, Australia. He joined the council in 1927.

PLATO MALOZEMOFF, former vice-president of Newmont Mining Corp., was elected president of the corporation at a meeting of the directors on December 15. He succeeds Fred Searls, Jr., who was made chairman of the board.

A. H. MCNAB has been elected chairman and chief executive officer of Magma Copper Co., and of its subsidiary, San Manuel Copper Corp. He is succeeded as president of both concerns by Wesley P. Goss, former vice-president and general manager of the two organizations.

ALAN M. BATEMAN, Silliman Professor of geology at Yale University, has just returned from a six weeks' stay in India where he attended the India Science Congress and visited various institutions of learning and mineral deposits as a guest of the Indian Government.

LAWRENCE D. SCHMIDT, formerly with the U. S. Bureau of Mines, is Director of Research, Semet-Solvay Div., Allied Chemical & Dye Corp., New York.

JOHN D. RIDGE, associate professor and chief of the Div. of Mineral Economics, Pennsylvania State College, has been named professor of mineral economics and assistant dean, School of Mineral Industries, in charge of resident instruction. He will also continue as chief of the Div. of Mineral Economics.

LLOYD ALLEN THOMAS, geologist, is with Magma Copper Co., Superior, Ariz.

EDWARD STEIDLE, Dean Emeritus, School of Mineral Industries, Pennsylvania State College, is chairman of the Federal Coal Mine Safety Board of Review. He was appointed to the position by President Eisenhower for a term to expire on July 15, 1955.

RALPH DIGMAN died of poliomyelitis on December 20th.

HENRY DEWITT SMITH is President-elect of the American Institute of Mining Engineers.

W. D. JOHNSTON, JR., chief of the Foreign Section of the U. S. Geological Survey is presently in Brazil in connection with cooperative geological work between the U. S Geological Survey and the Government of Brazil.

THE NATIONAL SCIENCE FOUNDATION'S PANEL ON MINERALS RESEARCH has appointed the following chairmen and associate chairmen for some of the subcommittees set up to date: for Fundamental Geochemistry, R. M. GARRELS and J. LAWRENCE KULP; for Geophysics, B. F. HOWELL, JR. and FRANCIS BIRCH; for Scientific Manpower, HOWARD A. MEYERHOFF and CHARLES B. HUNT; for Fundamental Geological Research, FREDERICK S. TURNEAURE. The other members of each committee are at present under consideration.

THOMAS B. NOLAN was awarded the K. C. Li Gold Medal at a ceremony held at the Faculty Club of Columbia University on February 12.

ANDREW V. CORRY, Minerals Attaché, U. S. Embassy, New Delhi, India, is returning to the U. S. in March.

JOHN E. SANDERS has been appointed instructor in the Department of Geology, Yale University, commencing September, 1954.

C. J. SULLIVAN, formerly of Australia, has been appointed to Kennco Exploration, Ltd., Toronto, Canada.

OLAF N. ROVE has resigned from the U. S. Geological Survey to enter private industry.

LOUIS G. GRATON can be reached at his new address: 182 Brattle Street, Cambridge 38, Mass.

RICHARD V. WYMAN has resigned from the New Jersey Zinc Co. and is now chief geologist of Western Gold & Uranium Inc. at the Silver Reef uranium mines. Leeds, Utah.

V. A. GORSKY, consultant mining engineer and metallurgist, has joined the geological department, University of Natal in Durban, South Africa, doing research work and lecturing on engineering geology.

C. J. ABRAMS, general manager of western operations for the Climax Molybdenum Co., Denver, has been made head of a newly created exploration division. Succeeding Mr. Abrams is Frank Coolbaugh, resident manager of the Climax, Colo., operations.

FREDERICK D. WRIGHT, research mining engineer, U. S. Bureau of Mines, has left on a six month's leave of absence for Durango, Mexico, where he will have charge of the operations at the San Martin mine near Sombrerete.

J. PARNELL CAULFIELD, general manager, Western Mining Div., Kennecott Copper Corp., has been elected president of the Utah Mining Assn. for 1954.

MACK C. LAKE has retired as president of Orinoco Mining Co., a U. S. Steel Corp. subsidiary, but continues in a consulting capacity. Mr. Lake joined U. S. Steel in 1945 and directed exploration which led to the discovery in 1947 of the iron ore deposits in Cerro Bolivar, Venezuela. He became president of Orinoco in 1949 when the subsidiary was formed. He is succeeded by Francis Thomas, vice-president.

G. F. JOKLIK, on leave of absence from the Bureau of Mineral Resources, Canberra, Australia, is studying geology at the University of Columbia on a Fulbright scholarship.

TRUMAN H. KUHN, professor of geology and dean of the Graduate School, Colorado School of Mines, recently returned from Turkey where he estimated chromium reserves for a Turkish mining company.

The Economic Geology Publishing Company is planning to celebrate the 50th Anniversary of the founding of its journal Economic Geology in 1905 by a forthcoming "50th Anniversary Volume" to be published in 1955. This book will consist of 33 broad review articles covering various fields of interest in economic geology, contributed by 38 outstanding authors. It will appear in two volumes of approximately 500 pages each. The exact date of publication will be announced later. The exact price cannot be set now but it will be held as low as possible, with a lower price for regular and student subscribers to the Journal. It will be helpful in determining the size of the edition if those interested in procuring copies would advise, without committment at this time, Dr. M. M. Leighton, Business Manager, Urbana, Illinois, of their expected intention.